Switching and Extension of a [c2]Daisy-Chain Dimer Polymer

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Supporting Information

Experimental procedures and characterization data (^{1}H and ^{13}C and 2D NMR, IR, HRMS, GPC) for all compounds and their precursors.

General Information. NMR spectra were obtained on either a Mercury 300 MHz spectrometer, an INOVA 500 MHz spectrometer equipped with an AutoX broadband probe with z-gradients, or an INOVA 600 MHz spectrometer equipped with an inverse HCN triple resonance probe with x,y,and z-gradients. All spectrometers were running Varian VNMRJ software. Chemical shifts for both ^{1}H and ^{13}C spectra are reported in per million (ppm) relative to Si(CH3)4 (δ=0) and referenced internally to the proteo solvent resonance. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (qt), septuptlet (sp), multiplet (m), and broad (br). MestReNova NMR 5.3.2 software was used to analyze all NMR spectra. Molecular mass calculations were performed with ChemBioDraw Ultra 11.0.1 (Cambridge Scientific). Mass spectrometry measurements (FAB, EI, and MALDI) were performed by the California Institute of Technology Mass Spectrometry Facility. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization was performed using UV and iodine stain. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. Gel permeation chromatography (GPC) was carried out in 0.2 M LiBr in DMF

on two I-series Mixed Bed Low MW ViscoGel columns (Viscotek) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and *dn/dc* values were obtained for each injection assuming 100% mass elution from the columns. IR was obtained on a Perkin-Elmer BX-II FTIR spectrometer using thin-film techniques on NaCl plates.

Materials and Methods. Anhydrous N,N-dimethylformamide (DMF) was obtained from Acros (99.8% pure, Acroseal). Dry tetrahydrofuran (THF), toluene, and dichloromethane (DCM) were purified by passage through solvent purification columns.[1] All water was deionized. 6-Bromo-1-hexanol (**10**, 97%), syringaldehyde (**12**, 98%), 5-bromo-1-pentene (**17**, 95%), protocatechuic acid ethyl ester (**20**, 97%) 4'-Hydroxy-4-biphenylcarboxylic acid (**24**, 99%), and 1,4-diethynylbenzene (96%) were purchased from Aldrich and used as received. Anhydrous potassium carbonate (J. T. Baker, 99.6%) was used as received. Grubbs 2nd Generation catalyst $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**) was obtained as a generous gift from Materia, Inc. All other compounds were purchased from Acros or Aldrich and used as received.

General Freeze-Pump-Thaw Procedure. A flask charged with reagents and solvent was frozen with liquid nitrogen. After the solution had frozen, the headspace of the flask was evacuated under vacuum. The flask was sealed and allowed to thaw to room temperature. The headspace of the flask was then backfilled with argon. The flask was sealed and the reaction mixture frozen again with liquid nitrogen. This process was repeated twice. On the third cycle, the solution was frozen and the headspace evacuated and backfilled with argon. Catalyst was quickly added to the top of the frozen solution, the headspace was again evacuated, and the solution allowed to warm to room temperature. The solution was backfilled with argon, refrozen, and subjected to another cycle for a total of four freeze-pump-thaw cycles.

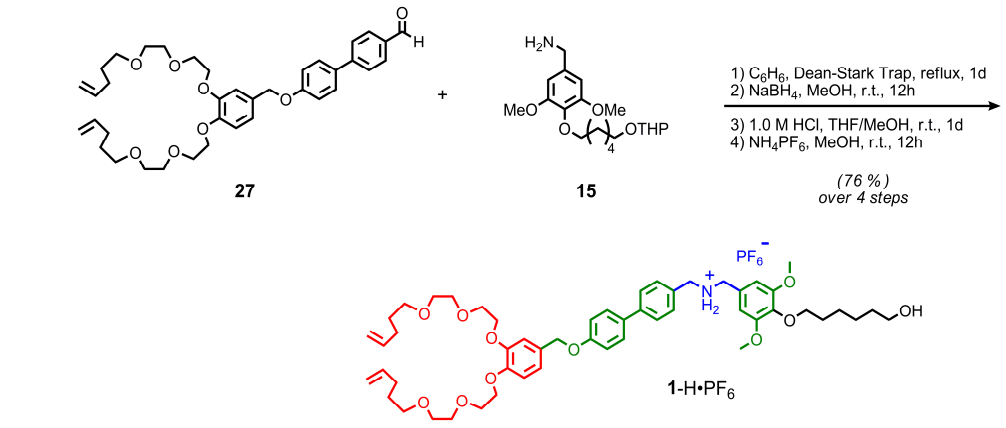
References:
1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

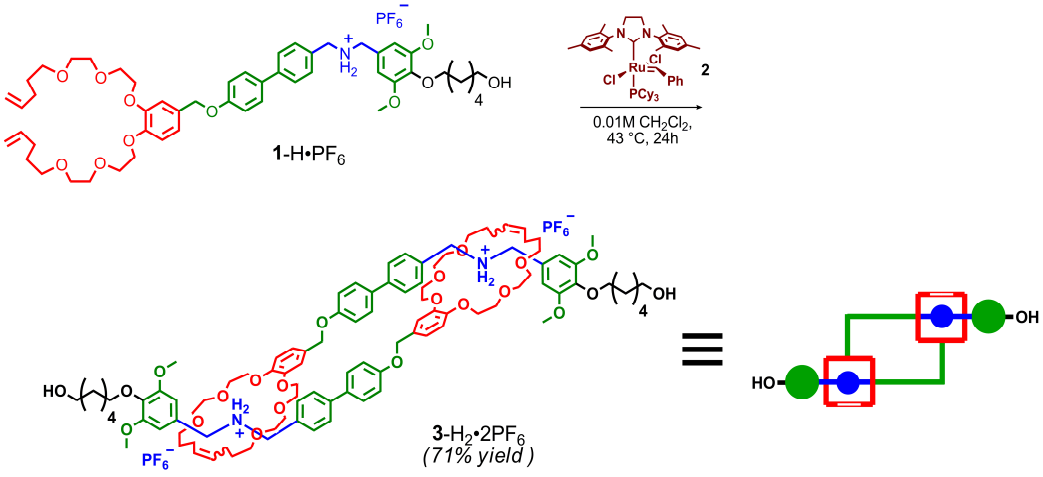
General Phenol Alkylation Procedure. To a cooled, flame-dried, 2-neck round bottom flask, equipped with a stir bar and fitted with a septum, water-jacketed reflux condenser, and vacuum adapter was added, under argon, 3 equivalents (relative to each mole of phenol) of anhydrous potassium carbonate, anhydrous DMF (to make a ~0.1 M solution), and phenol at room temperature. To this stirring mixture was added the alkylating agent dissolved in a minimal amount of DMF. The reaction was heated to 90 °C in an oil bath for 2 to 3 days, and, upon completion, was stopped by cooling to room temperature. The reaction mixture was poured into a separatory funnel, and partitioned between water (5x original volume of DMF) and ethyl acetate (1x original volume of DMF). The aqueous layer was extracted three times with fresh portions of ethyl acetate (1x original volume of DMF), and the combined organic layers were washed three times with fresh portions of water and brine (1x original volume of DMF). The washed organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$), filtered through filter paper, and evaporated to dryness under reduced pressure to give the alkylation product. Purification was achieved by silica gel flash chromatography using various eluents.

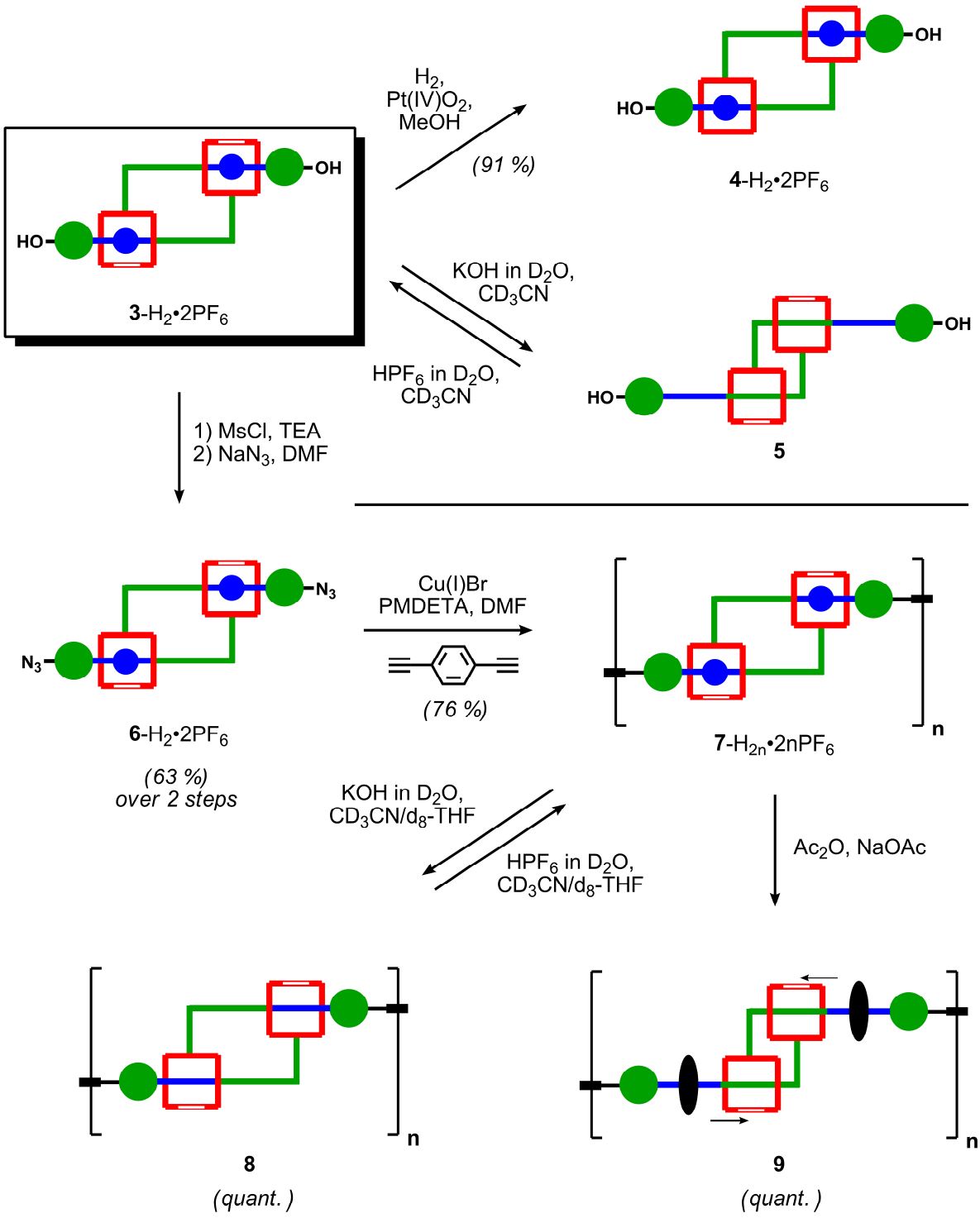
General Lithium Aluminum Hydride Reduction Procedure. To a cooled, flame-dried 2-neck flask, equipped with a stir bar and fitted with a septum, water-jacketed reflux condenser, and vacuum adapter was added, under argon and at 0 °C, 3 equivalents of lithium aluminum hydride (LAH) powder (95+%), dry THF, and, slowly, 1 equivalent of ester, acid, aldehyde, or nitrile dissolved in a minimal amount of dry THF. The reaction was heated to 87 °C overnight in an oil bath. To quench the reaction mixture, the oil bath was removed and the reaction cooled to 0 °C. Water (1 ml per gram of LAH) was added very slowly to the stirring mixture, followed by very slow addition of a 15 % sodium hydroxide solution (1 ml per gram of LAH). Water (3 ml per gram of LAH) was added very rapidly, and the resulting slurry was allowed to stir for 4 hours at room temperature. After this time, a large excess of celite and anhydrous $MgSO_4$ was added, and the mixture allowed to stir for an additional hour. The reaction was filtered, and the solvent removed by rotary evaporation. The product was redissolved in organic solvent (0.5x original volume of THF), and partitioned with water (1x original volume of THF) in a separatory

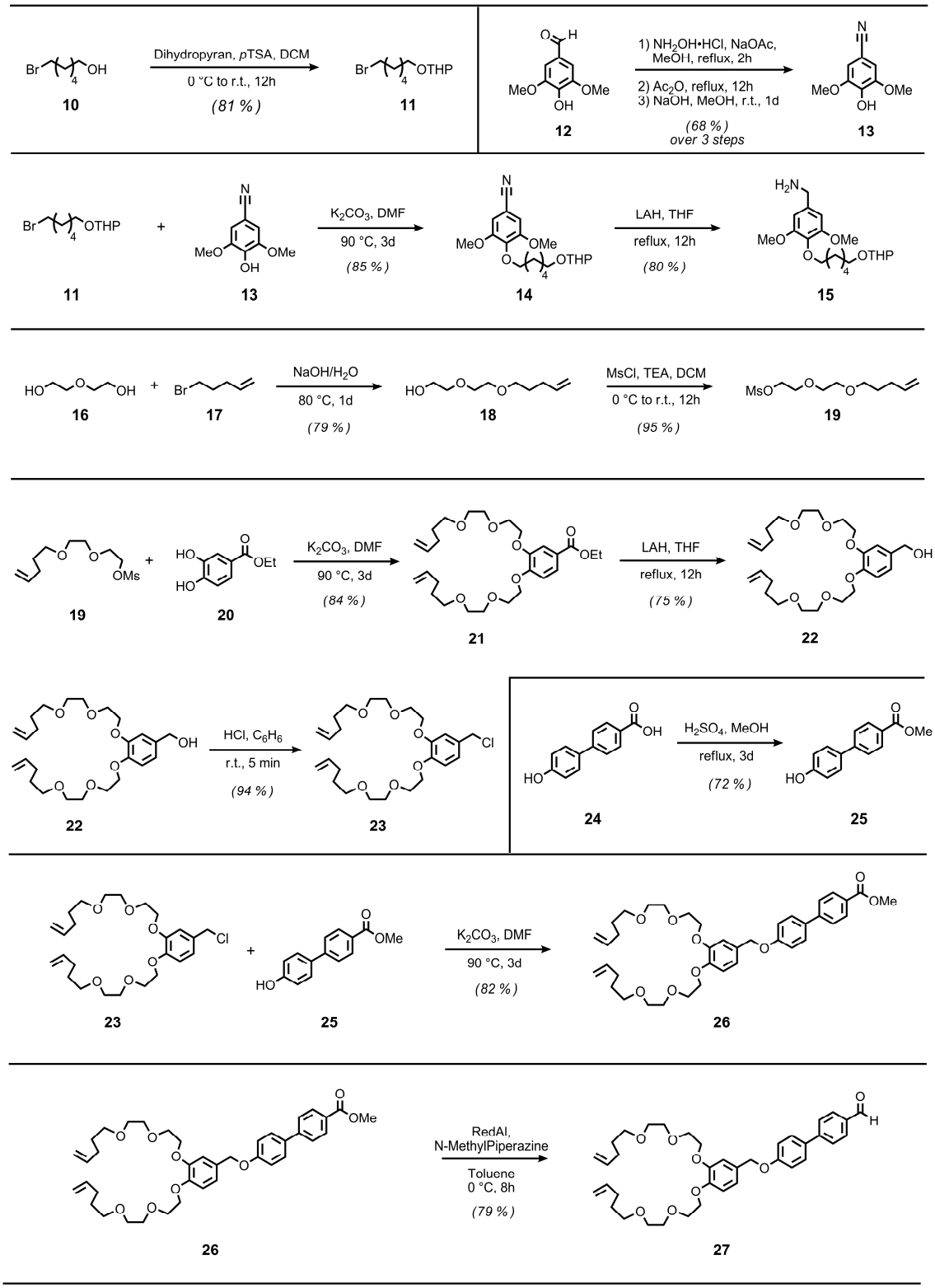
funnel. The water layer was extracted three times with fresh solvent (0.25x original volume of THF), and the combined organic layer was washed with two fresh portions of water (0.5x original volume of THF), dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness under reduced pressure to give the reduced product. The products were used with no further purification, or purified via specified protocols.

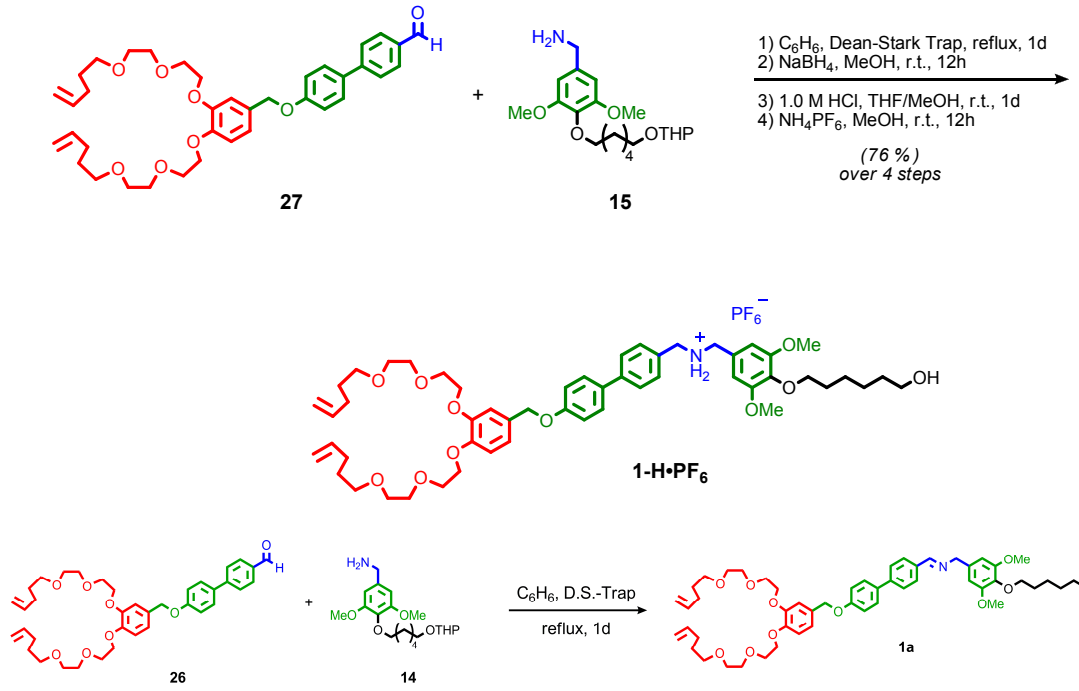
EXPERIMENTAL SECTION



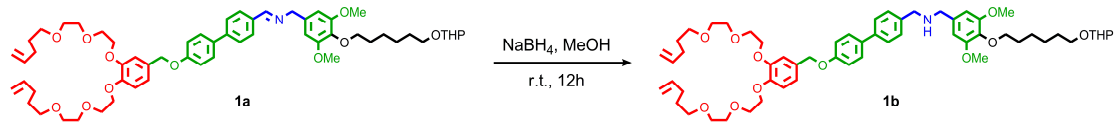



H2,
Pt(IV)O2,
MeOH
(91 %)
OH
HO
4-H2•2PF6
3-H2•2PF6
KOH in D2O,
CD3CN
HPF6 in D2O,
CD3CN
5
1) MsCl, TEA
2) NaN3, DMF
N3
6-H2•2PF6
(63 %)
over 2 steps
Cu(I)Br
PMDETA, DMF
(76 %)
7-H2n•2nPF6
n
KOH in D2O,
CD3CN/d8-THF
HPF6 in D2O,
CD3CN/d8-THF
Ac2O, NaOAc
8
(quant.)
9
(quant.)


Dihydropyran, pTSA, DCM
0 °C to r.t., 12h
(81 %)
10
11
1) NH2OH•HCl, NaOAc, MeOH, reflux, 2h
2) Ac2O, reflux, 12h
3) NaOH, MeOH, r.t., 1d
(68 %) over 3 steps
12
13
K2CO3, DMF
90 °C, 3d
(85 %)
14
LAH, THF
reflux, 12h
(80 %)
15
NaOH/H2O
80 °C, 1d
(79 %)
16
17
18
MsCl, TEA, DCM
0 °C to r.t., 12h
(95 %)
19
K2CO3, DMF
90 °C, 3d
(84 %)
20
21
LAH, THF
reflux, 12h
(75 %)
22
HCl, C6H6
r.t., 5 min
(94 %)
23
H2SO4, MeOH
reflux, 3d
(72 %)
24
25
K2CO3, DMF
90 °C, 3d
(82 %)
26
RedAl, N-MethylPiperazine
Toluene
0 °C, 8h
(79 %)
27

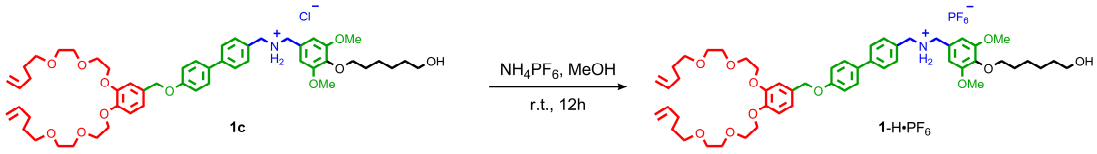


Self-Complimentary Macromer (1-H·PF_6). A flask equipped with a stir bar was charged with **27** (6.8249 g, 10.79 mmol, 1 eq), **15** (3.9635 g, 10.79 mmol, 1 eq), and benzene (250 ml). The flask was fitted with a Dean-Stark trap and reflux condenser, and heated to 100 °C. The trap was flushed several times over the course of the reaction. After 1 day, the reaction was cooled to room temperature and the benzene removed under reduced pressure to give imine **1a** as a viscous oil (10.59 g).



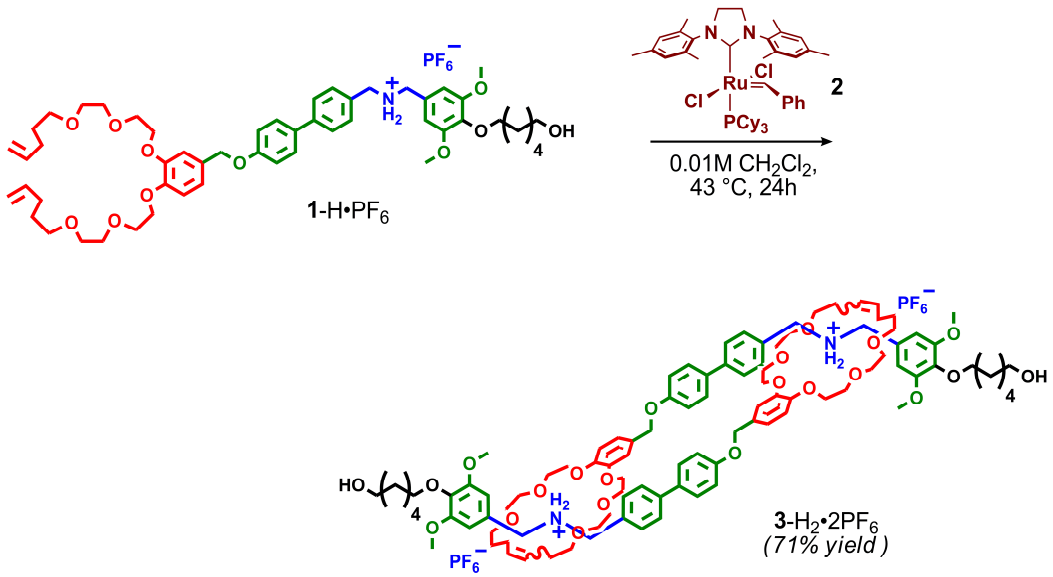
Imine **1a** (10.59 g) was dissolved in methanol (108 ml), and sodium borohydride (1.2241 g, 32.37 mmol) was added to the reaction. Stirring was continued at room temperature for 12 hours. The methanol was removed under reduced pressure, and the residue dissolved in DCM and transferred to a separatory funnel. Water was added, and the organic layer was rinsed three times with fresh portions of water. The organic layer was then dried over magnesium sulfate, filtered, and concentrated under reduced pressure, giving amine **1b** as a thick oil (10.3 g).

The amine **1b** (10.3 g) was dissolved in methanol (20 ml) and THF (100 ml), and to this mixture was added 1.0 M hydrochloric acid (155 ml, in water). This mixture was allowed to stir for one day, poured into a separatory funnel, and diluted with water and DCM. The water layer was extracted three times with fresh DCM and the combined organic layers were washed another two times with water, dried over magnesium sulfate, filtered, and evaporated to dryness under reduced pressure, giving ammonium-alcohol **1c** as a waxy solid (7.9 g).



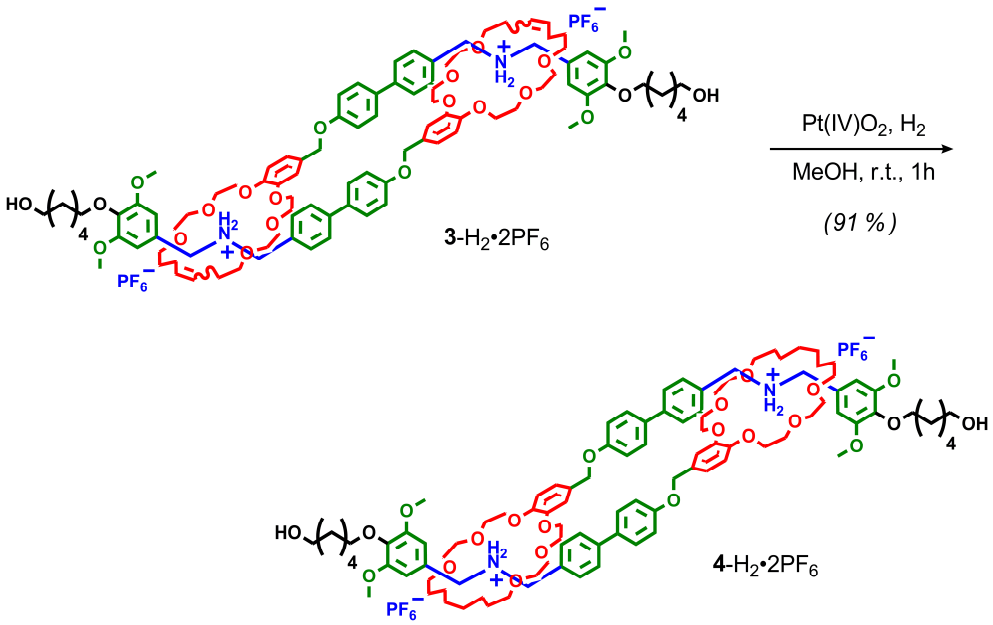
The compound was redissolved in methanol (150 ml), and ammonium hexafluorophosphate (13.7485 g, 84.34 mmol) was added. The reaction mixture was allowed to stir overnight, and was halted by evaporation of methanol under reduced pressure. The residue was dissolved in DCM, poured into a separatory funnel, and diluted with water. The organic layer was washed several times with fresh water, poured through filter paper, and evaporated to dryness under reduced pressure. Flash chromatography (SiO_2: gradient from 2%, then 2.5%, then 10% DCM to methanol eluent) gave **1**-H·PF_6 (8.6 g, 76% yield over 4 steps) as a pale-yellow waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (m, 6H), 6.91 (m, 4H), 6.78 (s, 1H), 6.70 (s, 2H), 5.76 (m, 2H), 5.05-4.86 (m, 4H), 4.74 (s, 2H), 4.48-3.98 (m, 4H), 3.91 (t, J = 6.50 Hz, 2H), 3.88-3.66 (m, 16H), 3.66-3.42 (m, 12H), 2.08 (m, 4H), 1.67 (sp, J = 1.67 Hz, 4H), 1.58-1.27 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.42, 153.70, 146.50, 145.99, 141.44, 137.88, 137.72, 137.44, 131.86, 130.52, 130.03, 128.23, 127.82, 126.48, 126.35, 119.65, 115.14, 114.92, 112.30, 110.80, 105.89, 73.28, 71.18, 71.02, 70.94, 70.72, 69.85, 69.76, 69.53, 69.34, 68.53, 67.66, 62.64, 56.14, 52.41, 32.47, 30.08, 30.01, 29.86, 28.58, 28.46,

25.49, 25.38. HRMS-FAB (m/z): [M – PF_6] calcd for $C_{53}H_{74}NO_{11}$, 900.5262; found, 900.5245.



[c2]Daisy-chain Dimer (3-H_2·2PF_6). A cooled, flame-dried flask equipped with a stir bar, gas port, and septum was charged, under argon, with **1**-H·PF_6 (10.00 g, 9.56 mmol, 1 eq) and dry DCM (960 ml, 0.01 M). This mixture was sparged with argon for 30 minutes, and catalyst (H_2IMes)(PCy_3)(Cl)$_2$Ru=CHPh **2** (406 mg, 0.478 mmol, 5 mol %) was added. The reaction was heated to 43 °C for 24 hours and was then quenched by addition of 5 ml of ethyl vinyl ether, which was allowed to stir for 30 minutes at elevated temperature. The solvent was removed under reduced pressure to give crude **3**-H_2·2PF_6 as a brown foam (9.2650 g, 91.4% recovered). A 100.0 mg portion of the foam was purified by flash chromatography (SiO_2: gradient from pure DCM to 0.5% methanol in DCM to 1.0% methanol in DCM to 2% methanol in DCM to 5% methanol in DCM) to afford pure **3**-H_2·2PF_6 as a white foam (77.6 mg, 71% overall isolated yield). Note: see ^{1}H spectra for full assignment. ^{1}H NMR (600 MHz, CD_3CN): δ 8.10 (br s, 2H), 7.75 (br s, 2H), 7.48-7.35 (m, 4H), 7.30-7.12 (m, 8H), 7.09 (d, J = 7.6 Hz, 1H), 7.02-6.75 (m, 11H), 6.38 (m, 1H), 6.25 (m, 1H), 5.75-5.39 (m, 4H), 4.88-3.12 (br m, 72H), 2.44 (t, J = 5.3 Hz, 2H), 2.41-1.99 (br m, 8H), 1.91-1.55 (m, 8H), 1.67 (qt, J = 7.0 Hz, 4H), 1.54-1.43 (m, 8H), 1.41-1.32 (m, 4H). ^{13}C NMR (126 MHz, CD_3CN): δ 159.96, 159.87, 155.30, 147.41, 147.26, 146.89, 146.81, 142.47, 139.18, 133.46, 133.36, 132.78, 132.69, 132.06,

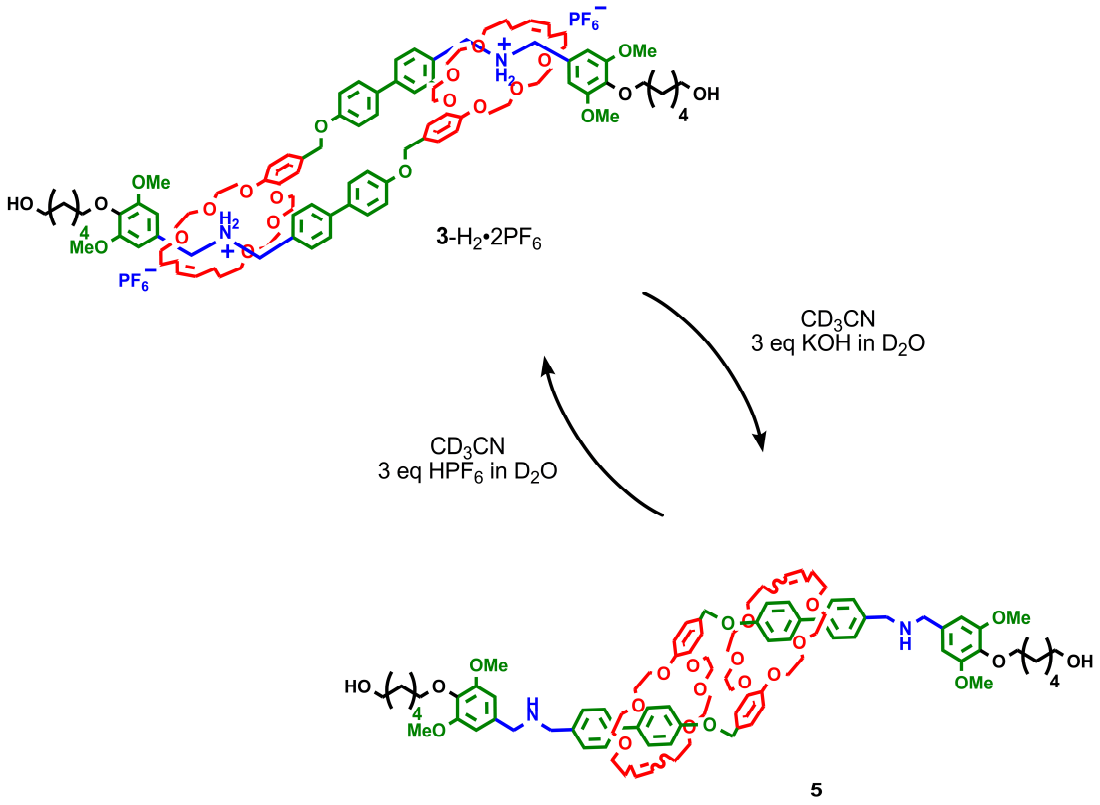
132.01, 131.93, 131.59, 131.48, 131.33, 131.27, 130.90, 130.85, 130.25, 129.30, 129.27, 128.46, 127.43, 127.29, 120.35, 119.82, 116.20, 116.16, 113.52, 113.24, 111.42, 111.02, 107.71, 107.27, 74.31, 73.45, 73.25, 73.07, 72.85, 72.80, 72.51, 72.41, 72.11, 72.05, 71.41, 71.23, 71.15, 71.00, 70.96, 70.77, 70.56, 70.48, 69.72, 69.46, 69.11, 68.90, 62.97, 57.30, 57.27, 53.66, 53.43, 33.98, 31.79, 31.75, 31.25, 30.44, 30.35, 29.71, 29.67, 29.58, 29.19, 29.09, 29.07, 26.93, 26.80, 26.66, 25.95. FTIR (NaCl, cm^{-1}): 3594.29, 3445.56, 3143.46, 3008.55, 2936.49, 2870.07, 2625.68, 2249.01, 1949.63, 1721.96, 1607.67, 1594.00, 1514.17, 1502.65, 1463.46, 1433.21, 1391.50, 1372.07, 1354.31, 1334.36, 1291.77, 1249.20, 1195.92, 1181.75, 1162.97, 1128.93, 1100.34, 1050.97, 993.38, 973.95, 948.94, 913.43, 842.34, 780.57, 763.77, 730.64, 697.31, 673.00, 647.63, 619.96. ESI-TOF MS (m/z): $[M + 2H - 2PF_6]^{+2}$ calcd for $C_{51}H_{70}NO_{11}$, 872.9966; found 872.9941.



Saturated [c2]Daisy-chain Dimer (4-H_2·2PF_6). To a round bottom flask equipped with a stir bar was added **3**-H_2·2PF_6 (40.0 mg, 19.6 μmol, 1 eq) and methanol (25 ml). The dimer was dissolved in the methanol via heating, then allowed to cool to room temperature. To the solution, "Adam's Catalyst" platinum(IV) oxide (89 mg, 0.393 mmol, 20 eq) was added in one portion. The flask was sealed with a septum, and, with stirring, was vigorously sparged with hydrogen gas for 15 minutes. The catalyst changed color from brown to black-gray. After the sparging was complete, a balloon of hydrogen was placed into the septum, and a positive pressure of hydrogen was maintained throughout the course of the reaction. The reaction was stirred very vigorously for one hour then filtered through a pad of celite to give the saturated dimer **4**-H_2·2PF_6 as a white solid (36.4 mg, 91% yield). (see ^{1}H of **3**-H_2·2PF_6 for proton letter assignments) ^{1}H NMR (600 MHz, CD_3CN): δ 8.10 (br s, 2H), 7.75 (br s, 2H), 7.45 (d, J = 8.7 Hz, 1.6H, $H_{n\ m}$), 7.41 (d, J = 8.7 Hz, 2.4H, $H_{n\ r}$), 7.30-7.24 (m, 4H, H_p), 7.21 (d, J = 8.2 Hz, 1.6H, $H_{q\ m}$), 7.17 (d, J = 8.2 Hz, 2.4H, $H_{q\ r}$), 7.8 (d, J = 6.7 Hz, 0.9H, $H_{l\ m}$), 6.98 (d, J = 8.5 Hz, 0.9H, $H_{k\ m}$), 6.96-6.93 (s + d, 5.2H, H_r + $H_{l\ r}$), 6.89 (d, J = 8.5 Hz, 1.3H, $H_{k\ r}$), 6.86 (d, J = 8.7 Hz, 1.6H, $H_{o\ m}$), 6.82 (d, J = 8.7 Hz, 2.4H, $H_{o\ r}$), 6.40 (m, 1.2 H, $H_{b\ r}$), 6.26 (m, 0.8H, $H_{b\ r}$), 4.85-4.25 (m, 12H, H_a + H_j), 4.15-3.40 (m + $t_{3.95}$ + $s_{3.79}$ + $t_{3.47}$, 60H, [m = H_f -H_j] + [$t_{3.95}$ = H_t] + [$s_{3.79}$ = H_s] + [$t_{3.47}$ = H_y]), 2.44 (t, J = 5.3 Hz, 2H, H_z), 1.73-1.33 (br m, 40 H, H_u -H_x + H_c -H_e). ^{13}C NMR (126 MHz, CD_3CN): δ 159.96, 159.87, 155.29, 147.34,

147.24, 146.71, 146.66, 142.41, 142.28, 139.05, 133.34, 133.28, 131.98, 131.82, 131.60, 131.47, 130.23, 129.26, 128.49, 128.47, 127.44, 127.31, 120.24, 119.83, 118.69, 116.13, 113.35, 113.07, 111.31, 111.02, 107.32, 74.28, 73.44, 73.19, 73.15, 72.88, 72.83, 71.76, 71.36, 71.11, 70.12, 69.93, 69.68, 69.40, 68.95, 68.78, 62.95, 57.29, 53.80, 53.73, 33.97, 31.24, 30.88, 30.83, 30.53, 30.49, 29.10, 29.08, 28.96, 26.92, 26.79, 26.74, 26.73, 26.57, 26.55. FTIR (NaCl, cm^{-1}): 3593.99, 3433.21, 3137.28, 2933.11, 2860.90, 1952.15, 1593.24, 1514.07, 1501.41, 1463.66, 1435.55, 1393.10, 1372.52, 1353.85, 1334.80, 1293.11, 1248.93, 1196.12, 1181.25, 1162.76, 1128.62, 1099.00, 1048.90, 1001.31, 974.66, 906.59, 842.20, 780.29, 763.75, 735.51, 701.04, 672.30, 619.80, 588.82, 557.65, 528.46. ESI-TOF MS (m/z): $[M - PF_6]^{1+}$ calcd for $C_{102}H_{144}N_2O_{22}F_6P$, 1893.9853; found, 1893.9867.

Crystals suitable for x-ray diffraction were obtained for the mesoform via slow evaporation of a solution of **4**-H_2·$2PF_6$ (10.7 mg) in 3:3:1 hexanes:ethyl acetate:acetonitrile (0.5 ml, 0.5 ml, 0.17 ml, respectively). The racemic mixture remained soluble and did not crystallize (see ^{1}H NMR of each diastereomer in spectra section). The solid-state structure was deposited in the CCDC: 734570. See the CIF file for complete details.

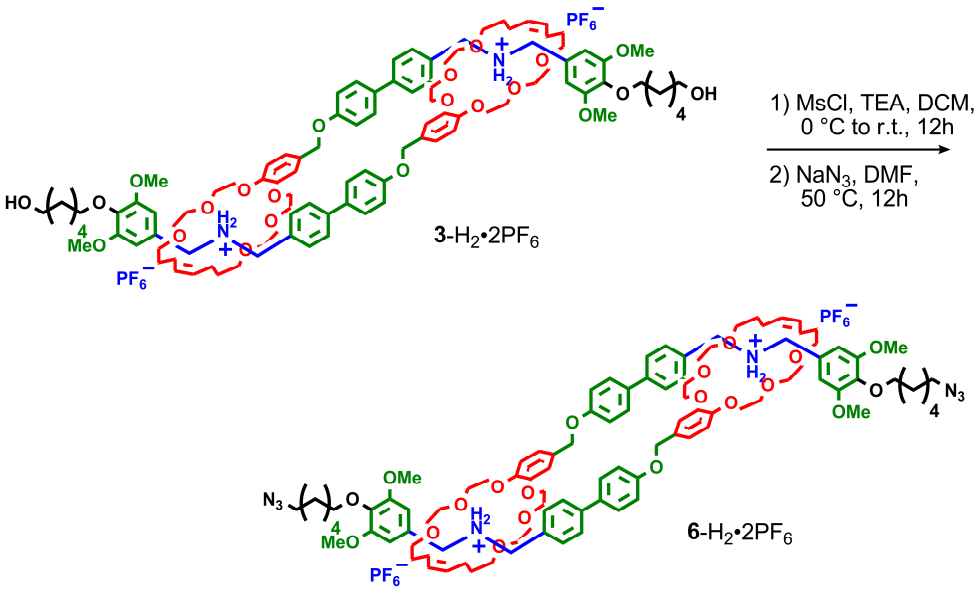


Deprotonated [c2]Daisy-chain Dimer (5). To a vial was added **3**-H_2·2PF_6 (44.3 mg, 21.8 μmol, 1 eq) and deuterated acetonitrile (0.5 ml), and this solution was transferred via pipet to a 5mm NMR tube. To a separate vial was added potassium hydroxide (122 mg, 2.18 mmol, 100 eq) and deuterium oxide (0.50 ml). Using a 25 μl syringe (Hamilton 1700 Series Gastight Syringe), 5 μl injections (total of 3 injections) of the KOH/D_2O solution was added to the NMR tube. After each injection, the tube was vigorously shaken for 10-15 seconds, and then reinserted into the spectrometer. Deprotonation was complete after addition of 3 equivalents of potassium hydroxide, giving **5**. The sample remained stable for 36h, with an unchanged ^{1}H NMR spectrum, and was subjected to reprotonation with no purification. ^{1}H NMR (600 MHz, CD_3CN): δ 7.75-7.30 (br m, 5H), 7.30-7.15 (m, 4H), 7.15-6.19 (br m, 17H), 5.85-5.15 (br m, 4H), 4.87-3.15 (br m, 74H), 2.45-2.00 (br m, 8H), 1.83-1.53 (br m, 12H), 1.53-1.42 (m, 8H), 1.34 (qt, 4H). ^{13}C NMR (126 MHz, CD_3CN): δ 159.48, 154.59, 148.98, 148.78, 147.07, 141.84, 140.98, 140.10, 139.12, 136.49, 134.58, 131.68, 131.10, 130.54, 130.02, 128.94, 126.69, 120.72, 116.51, 116.18, 112.85, 107.55, 107.29, 74.05, 72.76, 71.85, 71.49, 71.04, 70.77, 70.60, 70.42,

70.01, 69.70, 69.03, 68.47, 62.72, 56.99, 56.89, 54.86, 53.48, 33.74, 31.73, 31.10, 30.40, 29.71, 27.68, 26.81, 26.66.

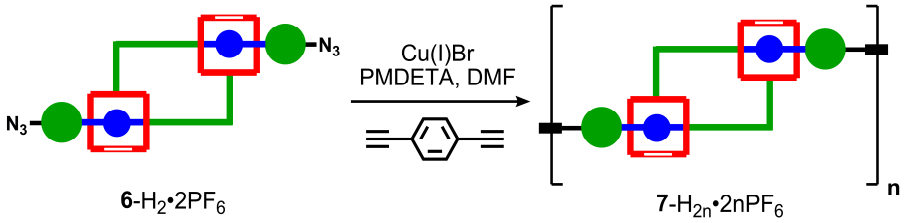
A third vial was charged with deuterium oxide (0.5 ml) and hexafluorophosphoric acid (296 µl, 2.18 mmol, 100 eq, 60 wt% in H_2O). Using the same 25 µl syringe, 5 µl injections (total of 3 injections) of this solution were added to the NMR tube containing **5**, restoring the ^{1}H NMR spectrum corresponding to **3**-H_2·$2PF_6$ and completing the "switching" of the dimer. (see ^{1}H NMR spectral information for **3**-H_2·$2PF_6$) Note: spectra were taken immediately after appropriate locking and shimming protocols with no extra time allowed for additional reaction. All deprotonation and reprotonation reactions were complete by the time the necessary NMR protocols were complete (< 3 min).

After the switching was complete, the NMR sample was transferred to a vial and the solvent was removed under reduced pressure. The residue was dissolved in DCM (10 ml), and water was added (20 ml). The aqueous layer was extracted with fresh DCM (2 x 5 ml), and the combined organic layer further washed with fresh water (2 x 5 ml). The organic layer was poured through filter paper, and the solvent removed via rotary evaporation to return **3**-H_2·$2PF_6$ (37.5 mg, 85% recovery). See ^{1}H NMR spectral characterization information for **3**-H_2·$2PF_6$.

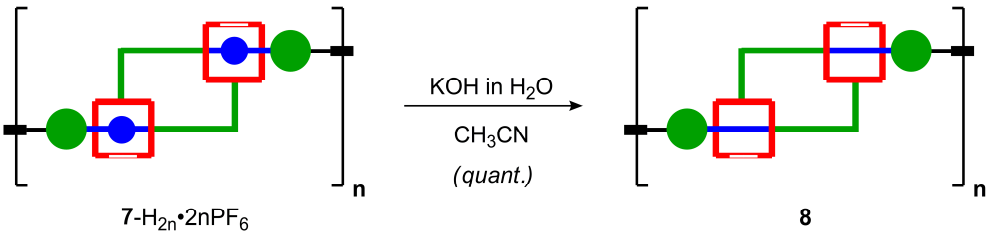


Diazide [c2]Daisy-chain Dimer (6-H_2·2PF_6). Crude **3**-H_2·PF_6 was mixed with ethyl acetate (5 ml) and vigorously sonicated for 15 minutes giving a tan oil. The ethyl acetate was decanted, and a fresh portion of ethyl acetate (5 ml) was added. The suspension was again sonicated vigorously for 15 minutes, and the ethyl acetate was decanted to give a pale tan powder. This terminal diol [c2]daisy-chain dimer **3**-H_2·PF_6 powder (2.58 g, 1.27 mmol, 1 eq) was dissolved in DCM (12.7 ml, 0.1 M) and triethylamine (1.1 ml, 7.62 mmol, 6 eq), and cooled to 0 °C. To this stirring solution, mesyl chloride (0.60 ml, 7.62 mmol, 6 eq) was added dropwise. The reaction was warmed to room temperature for 12h, then poured into a separatory funnel and diluted with water (100 ml) and DCM (25 ml). The aqueous layer was extracted with fresh DCM (2 x 25 ml), and the combined organic layer was washed with fresh water (50 ml). The organic layer was poured through filter paper, and evaporated to dryness. The resulting foam was mixed with ethyl acetate (5 ml) and subjected to sonication for 15 minutes. The ethyl acetate was decanted, and another 5 ml of fresh ethyl acetate was added. The suspension was sonicated for an additional 15 minutes, the ethyl acetate decanted, and the tan powder (2.24 g) was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (br m, 2H), 7.68 (br m, 2H), 7.43-7.27 (m, 4H), 7.22-7.02 (m, 8 H), 7.02-6.60 (m, 12 H), 6.32-6.10 (m, 2H), 5.68-5.21 (br m, 4 H), 5.05-4.01 (br m, 19 H), 3.96 (t, J = 6.4 Hz, 4H), 3.93-3.10 (br m, 48 H), 2.97 (s, 4H), 2.42-1.93 (br m, 8 H), 1.90-1.31 (br m, 24 H). The dimesylated dimer (2.24 g, 1.02 mmol, 1 eq) was added to a flame dried flask equipped

with a stir bar and under a positive argon atmosphere, and dry DMF (50 ml, 0.02 M) was added. Sodium azide (0.80 g, 12.24 mmol, 12 eq) was added in one portion, and the reaction mixture was heated to 50 °C for 12 h. The solution was poured into a separatory funnel and diluted with ethyl acetate (100 ml) and water (50 ml). The aqueous layer was extracted with fresh ethyl acetate (4 x 25 ml), and the combined organic layer was washed with fresh water (50 ml). The organic layer was poured through filter paper and evaporated to dryness. The resulting foam was sonicated with ethyl acetate (2 x 5 ml) to give **6**-$H_2 \cdot 2PF_6$ (1.67 g, 63%) as a pale tan foam that was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (br s, 2H), 7.65 (br s, 2H), 7.42-7.30 (m, 4H), 7.20-7.05 (m, 8H), 7.04 (d, J = 7.8 Hz, 1H), 6.95-6.70 (m, 11H), 6.28 (m, 1H), 6.15 (m, 1H), 5.61-5.29 (m, 4H), 4.82-3.18 (br m, 72H), 2.41-1.90 (br m, 8H), 1.90-1.35 (m, 24H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.54, 158.48, 154.06, 154.01, 145.86, 145.70, 145.31, 145.18, 141.53, 137.94, 131.62, 131.13, 130.61, 129.98, 128.24, 127.86, 127.13, 126.23, 119.28, 118.75, 114.97, 111.89, 111.75, 109.89, 109.57, 105.94, 105.30, 77.48, 77.23, 76.98, 73.57, 73.47, 71.83, 71.36, 71.22, 71.16, 71.04, 70.36, 70.04, 69.88, 69.80, 69.40, 69.30, 68.67, 68.25, 67.93, 67.90, 67.57, 67.47, 62.89, 56.44, 56.40, 52.31, 52.27, 51.51, 32.79, 30.62, 30.54, 30.11, 30.05, 29.18, 29.14, 28.90, 28.39, 28.34, 28.15, 28.01, 26.59, 25.71, 25.62, 25.52, 24.96, 24.91. FTIR (NaCl, cm^{-1}): 3956.56, 3659.54, 3592.45, 3141.56, 3008.82, 2936.76, 2623.29, 2530.03, 2360.09, 2343.93, 2096.21, 1952.38, 1593.87, 1505.34, 1455.83, 1393.37, 1372.65, 1353.86, 1335.16, 1249.54, 1195.47, 1181.54, 1162.53, 1125.38, 1048.91, 973.99, 898.13, 838.37, 779.95, 763.92, 734.50, 701.42, 672.28, 644.56, 632.82, 619.78, 588.90, 557.67, 528.21. ESI-TOF MS (m/z): $[M + 2H - 2PF_6]^{+2}$ calcd for $C_{51}H_{69}N_4O_{10}$, 897.5013; found 897.5054. GPC (DMF with 0.2 M LiBr): M_n = 3123 g/mol; M_w = 3868 g/mol; PDI = 1.24; dn/dc = 0.121 ; R_{gz} = n/a.

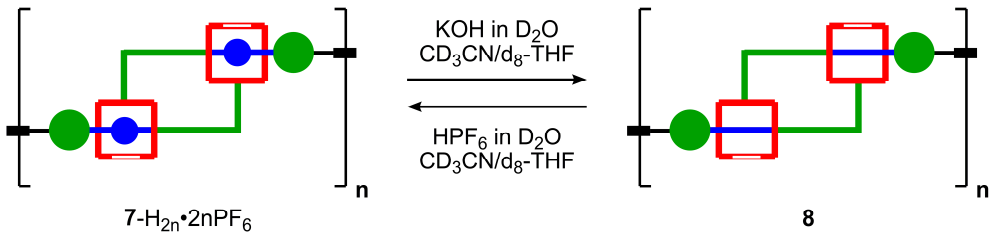


[c2]Daisy-chain Dimer Polymer (7-H_{2n}·2nPF_6). To a flame-dried vial equipped with a stir bar and septum cap was added 6-H_2·2PF_6 (75.0 mg, 35.9 μmol, 1 eq), 1,4-diethynylbenzene (4.5 mg, 35.9 μmol, 1 eq), *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine (37.5 μl, 179.8 μmol, 5 eq), and dry DMF (360 μl, 0.1M). This mixture was subjected to standard freeze-pump-thaw protocol, with addition of copper(I) bromide (26.4 mg, 179.8 μmol, 5 eq) after the 3rd freeze. After the 4th freeze-pump-thaw cycle was completed, the vial was placed in a 50 °C oil bath for 24h. The viscous reaction mixture was cooled to room temperature, and added dropwise to a stirring solution of methanol (40 ml). The precipitate was collected, dried, redissolved in dichloromethane (0.5 ml), and subjected to a second precipitation in fresh methanol (40 ml). The solid was collected and dried under reduced pressure to afford **7**-H_{2n}·2nPF_6 (60.4 mg, 76% yield) as an off-white powder. The product was used with no further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (br m, 4H), 7.91 (s, 4H), 7.82 (d, J = 7.7 Hz, 0.6 H), 7.70 (br s, 2H), 7.55 (d, J = 8.1 Hz, 0.6 H), 7.48-7.35 (m, 5H), 7.28-7.02 (m, 11H), 7.01-6.75 (m, 13H), 6.45-6.15 (m, 2H), 5.71-5.35 (m, 4H), 4.85-3.08 (br m, 88H), 2.50-1.80 (br m, 10H), 1.80-1.35 (m, 28H + HDO). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.12 (br m, 2H), 7.89 (s, 3H), 7.80 (d, J = 8.1 Hz, 0.5 H), 7.68 (br s, 2H), 7.53 (d, J = 7.3 Hz, 0.6 H), 7.48-7.30 (m, 4H), 7.28-7.08 (m, 9H), 7.05-6.60 (m, 11H), 6.40-6.10 (m, 2H), 5.71-5.35 (m, 4H), 4.90-3.08 (br m, 72H), 2.50-1.80 (br m, 12H), 1.80-1.35 (m, 22H + HDO). FTIR (NaCl, cm^{-1}): 3645.89, 3436.49, 3275.37, 3140.73, 3047.82, 3007.96, 2935.65, 2867.49, 2626.16, 2362.05, 2103.24, 1949.57, 1593.01, 1513.78, 1501.17, 1463.53, 1432.12, 1389.82, 1371.32, 1353.86, 1333.98, 1291.59, 1248.54, 1195.05, 1181.27, 1163.07, 1128.14, 1100.30, 1048.58, 973.32, 899.38, 842.74, 780.23, 763.80, 734.32, 700.48, 672.09, 644.03, 632.82, 619.48, 588.59, 557.58, 528.37. GPC (0.2 M LiBr in DMF): M_n = 47,940 g/mol; M_w = 141,100 g/mol; PDI = 2.94; dn/dc = 0.116; R_{gz} = 14.8 nm.



7-H_{2n}•2nPF_6 **8**

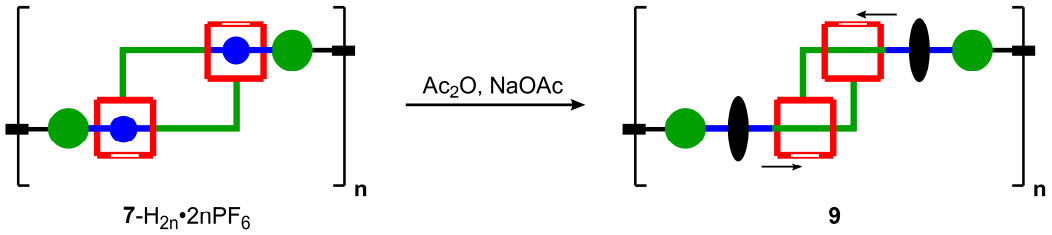
Deprotonation of [c2]Daisy-chain Dimer Polymer 7-H_{2n}·2nPF_6 (8). A vial was charged with **7**-H_{2n}·2nPF_6 (10 mg, 9 µmol, 1 eq) and acetonitrile (2 ml). To this mixture was added a 1.0 M solution of aqueous potassium hydroxide (1.8 ml), resulting in immediate precipitation of an off-white solid. The solution was decanted, and the solid was washed with fresh acetonitrile (2 x 2 ml). The deprotonated polymer **8** (9 mg, quant. yield) was analyzed with no further purification. The CD_2Cl_2 used in the NMR study was passed through a plug of basic alumina prior to addition to the deprotonated polymer sample. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.92-7.82 (m, 3.8H), 7.80 (d, J = 7.7 Hz, 0.4H), 7.53 (d, J = 7.9 Hz, 0.4H), 7.48-6.20 (m, 26H), 5.65-5.35 (m, 4H), 4.86-3.05 (br m, 72H), 2.55-1.55 (br m, 32H + H_2O signal). GPC (0.2 M LiBr in DMF): M_n = 41,680 g/mol; M_w = 125,800 g/mol; PDI = 3.02; dn/dc = 0.148; R_{gz} = 13.5 nm.



7-H_{2n}•2nPF_6 **8**

5x Switching of Polymer 7-H_{2n}·2nPF_6. A vial was charged with **7**-H_{2n}·2nPF_6 (11.6 mg, 5.3 µmol, 1 eq), and the polymer was dissolved in CD_3CN (0.4 ml) and loaded in an NMR tube. To the tube was added d_8-THF (0.4 ml), and the mixture was shaken vigorously for several seconds. The switching was performed via addition of a stock solution of KOH in D_2O (Stock Solution: 180 mg KOH in 0.5 ml D_2O; 5 µl injection volume, 6 eq) followed by vigorous shaking for 15 seconds to give **8**, and, after analysis, subsequent reprotonation via addition of a stock solution of HPF_6 in D_2O (450 µl 65% HPF_6 in 0.5 ml D_2O; 5 µl injection volume, 6 eq) to regenerate **7**-H_{2n}·2nPF_6. See **5** for

syringe specifications. After 5 cycles of deprotonation and reprotonation were completed, the polymer solution was transferred to a vial and the solvent was removed under reduced pressure. The residue was washed with water (2 x 2 ml) and dried under high vacuum, returning **7**-H_{2n}·2nPF_6 as a white solid (11.6 mg, quant. yield). Protonated Polymer: ^{1}H NMR (500 MHz, 1:1 CD_3CN/d_8-THF): δ 8.25-8.02 (m, 2.8 H), 7.92 (m, 2.6H), 7.85 (d, J = 8.0 Hz, 0.4H), 7.75 (br s, 2H), 7.53 (d, J = 8.1 Hz, 0.4H), 7.48-7.35 (m, 4H), 7.32-7.13 (m, 8H), 7.12-6.75 (12H), 6.47-6.18 (m, 2H), 5.75-5.35 (m, 4H), 4.86-3.15 (br m, 72H + d_8-THF), 2.55-1.70 (m, 18H + CD3CN + d_8-THF signal), 1.70-1.32 (m, 14H).

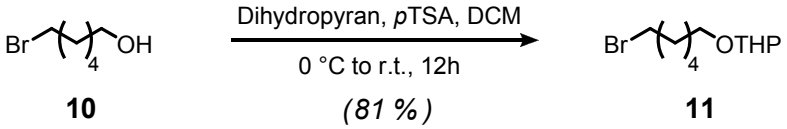


7-H_{2n}•2nPF_6 **9**

Acylated [c2]Daisy-chain Dimer Polymer (9). To a vial equipped with a stir bar was added **7**-H_{2n}·2nPF_6 (10.0 mg, 208 nmol, 1 eq), sodium acetate (18.5 mg, 225 µmol, 25 eq per ammonium), and acetic anhydride (500 µl). This solution was placed under a positive pressure of argon and heated to 90 °C for 2 hours. The acetic anhydride was removed under reduced pressure, and the resulting residue washed with water (3 x 2 ml) to give the acylated derivative **9** (9.1 mg, quant. yield) as an off white powder. The product was used with no further purification. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.82-7.68 (m, 5H), 7.67-7.48 (m, 8H), 7.48-6.67 (br m, 15H), 6.45-6.15 (m, 6H), 5.50-4.98 (m, 4H), 4.60-4.15 (m, 16H), 4.09-3.05 (br m, 62H), 2.50-1.55 (br m, 30H), 1.50-1.28 (m, 10H). GPC (0.2 M LiBr in DMF): M_n = 26,870 g/mol; M_w = 117,200 g/mol; PDI = 4.36; dn/dc = 0.133; R_{gz} = 21.8 nm.

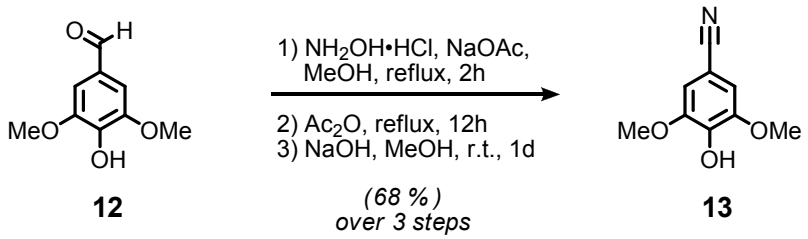
Note on GPC Analysis: All polymer GPC LS analyses were fitted using the Zimm Model. Though all polymers displayed limited solubility in the 0.2 M LiBr DMF eluent,

efforts to use an alternate eluent without salt (DMF or THF) generated chromatographs unsuitable for analysis due to severe polymer aggregation on the SEC columns.



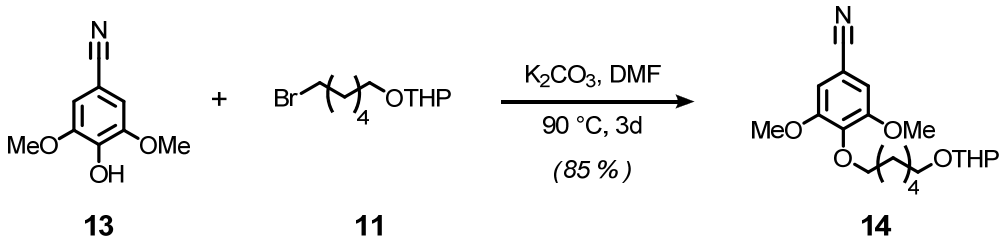
10 *(81 %)* **11**

2-(6-Bromohexyloxy)tetrahydro-*2H*-pyran (11). A cooled, flame-dried round bottom flask equipped with a stir bar and septum was charged, under argon and at 0 °C, with 6-bromo-1-hexanol **(10)** (7.6551 g, 42.28 mmol, 1 eq), dry DCM (10 ml), dihydropyran (4.25ml, 46.51 mmol, 1.1 eq), and *p*-toluenesulfonic acid (0.4030 g, 2.12 mmol, 5 mol %). The reaction was allowed to stir at room temperature overnight, and was quenched by diluting with water (50 ml) and DCM (50 ml) in a separatory funnel. The organic layer was washed three times with brine (3 x 50 ml), dried ($MgSO_4$), filtered, and evaporated to dryness under reduced pressure. Flash chromatography (SiO_2: 15:1 hexanes to ethyl acetate) gave **11** (9.0902 g, 81% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.56 (t, J = 2.75 Hz, 1H), 3.85 (m, 1H), 3.72 (m, 1H), 3.51 (m, 1H), 3.40 (m, 3H), 1.95-1.36 (br m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 99.05, 67.56, 62.54, 34.02, 32.92, 30.94, 29.73, 28.18, 25.67, 25.65, 19.87. HRMS-FAB (m/z): [M + H] calcd for $C_{11}H_{22}O_2Br$, 265.0803; found 265.0804.



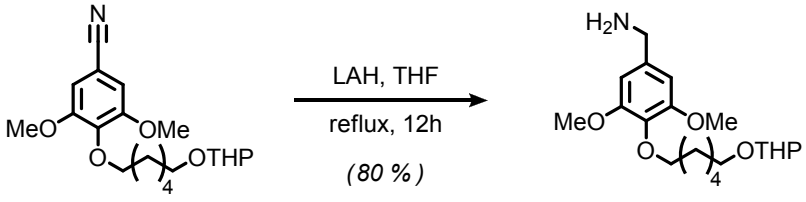
Nitrile Cap Fragment (13). To a flask fitted with a reflux condenser was added syringaldehyde **(12)** (5.0000 g, 27.44 mmol, 1 eq) and methanol. Sodium acetate (3.3999 g, 42.43 mmol, 1.51 eq) was added to the stirring solution, followed by hydroxylamine hydrochloride (2.8610 g, 41.16 mmol, 1.5 eq). The solution was heated to reflux for 2h, then cooled to room temperature. The methanol was removed under reduced pressure, and the residue redissolved in ethyl acetate (100 ml) and added to a separatory funnel. Brine (50 ml) and an aqueous solution of citric acid (23.1 g, 109.8 mmol, 4 eq in 220 ml water, 0.5 M) were added, and the aqueous layer was extracted twice more with fresh ethyl acetate (2 x 50 ml). The combined organic layer was washed with brine (2 x 50 ml), dried over magnesium sulfate, filtered, and evaporated to dryness under reduced pressure to give a yellow solid (5.1273 g, 95%). The oxime was dissolved in acetic anhydride (25 ml, 250 mmol, 10 eq) and heated to reflux for 1d. The acetic anhydride was removed under high vacuum, and the resulting black residue dissolved in ethyl acetate and mixed in a separatory funnel with saturated sodium bicarbonate and water. The aqueous layer was extracted with fresh ethyl acetate (2 x 100 ml), and the combined organic layers were dried over magnesium sulfate, filtered, and evaporated to dryness, giving a brown oil. Methanol (80 ml, 0.4 M) was added to the oil, followed by a 50 weight percent solution of sodium hydroxide (10.33 g, 250 mmol). After stirring overnight, the methanol was removed by rotary evaporation and the aqueous layer acidified with 2 M hydrochloric acid. Ethyl acetate was mixed with the aqueous layer, and the solution extracted with fresh ethyl acetate (3 x 50 ml). The combined organic layers were washed with water (2 x 100 ml), dried over magnesium sulfate, and evaporated under reduced pressure to give a thick oil that solidified upon standing. Purification was achieved by flash chromatography (SiO_2: gradient from 6:1 to 4:1 to 2:1 hexanes to acetone) to give **13** as an off-white crystalline solid (3.1574 g, 68%). ^{1}H NMR (600 MHz, Acetone-d_6): δ 8.20 (br s, 1H), 6.97 (s, 2H), 3.85 (s, 6H). ^{13}C NMR (75 MHz,

Acetone-d_6): δ 148.95, 141.51, 120.15, 110.41, 102.06, 56.91. HRMS-EI (m/z): [M + H] calcd for $C_9H_{10}NO_3$, 180.0661; found 180.0643.



13 **11** **14**

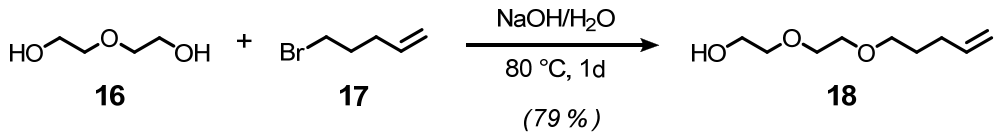
Alkylated Nitrile Cap Fragment (14). Standard alkylation conditions were used with **13** (2.8437 g, 15.87 mmol, 1eq), **11** (4.2089 g, 15.87 mmol, 1eq), K_2CO_3 (6.5802 g, 47.61 mmol, 3eq), and dry DMF (150 ml, 0.1M). The reaction was heated for 3 days, followed by extraction with ethyl acetate. Flash chromatography (SiO_2: 4:1 hexanes to acetone) gave **14** (4.9 g, 85% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (s, 2H), 4.49 (t, J = 2.75 Hz, 1H), 4.95 (t, J = 6.74 Hz, 2H), 3.80 (m, 1H), 3.78 (s, 6H), 3.65 (m, 1H), 3.41 (m, 1H), 3.31 (m, 1H), 1.91-1.32 (m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.83, 141.77, 119.06, 109.50, 106.45, 98.90, 73.65, 67.55, 62.39, 56.39, 30.82, 30.03, 29.75, 26.02, 25.64, 25.53, 19.76. HRMS-EI (m/z): [M + H] calcd for $C_{20}H_{29}NO_5$, 363.2046; found 363.2031.



14 **15**

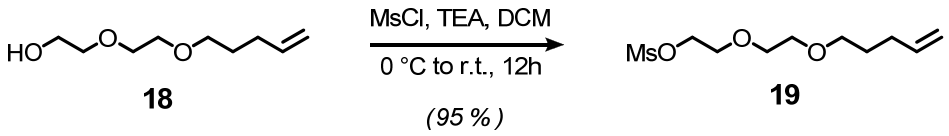
Alkylated Amine Cap Fragment (15). Standard LAH reduction conditions were used with **14** (4.9 g, 13.48 mmol, 1 eq), LAH (1.5349 g, 40.44 mmol, 3 eq), and dry THF (200 ml, 0.07 M). After heating overnight, the reaction was quenched, filtered, and the solvent removed under reduced pressure to give **15** (3.9635 g, 80% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.52 (s, 2H), 4.55 (t, J = 2.75 Hz, 1H), 3.92 (m, 2H), 3.84 (m, 1H),

3.82 (s, 6H), 3.80 (s, 2H), 3.72 (m, 1H), 3.47 (m, 1H), 3.37 (m, 1H), 1.86-1.26 (m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.58, 138.75, 136.09, 104.11, 98.89, 73.39, 67.66, 62.39, 56.15, 46.79, 30.84, 30.22, 30.08, 29.81, 26.13, 25.80, 25.56, 19.76. HRMS-FAB (m/z): [M + H] calcd for $C_{20}H_{34}O_5N$, 368.2437; found 368.2450.

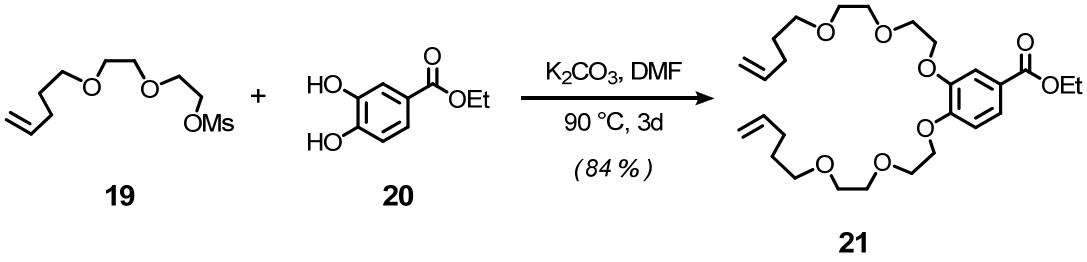


16 **17** **18**

2-(2-(Pent-4-enyloxy)ethoxy)ethanol (18). A flask equipped with a stir bar was charged with diethylene glycol **(16)** (637 ml, 6.71 moles, 20 eq) and 5-bromo-1-pentene **(17)** (50 g, 0.37 moles, 1 eq). A solution of sodium hydroxide and water (67.1 g NaOH, 1.68 moles, 5eq; 67 ml of H_2O) was added slowly over a period of one hour via an addition funnel, resulting in turbidity of the reaction mixture. The reaction was heated to 80 °C for one day, and after cooling to room temperature, the mixture was poured into a separatory funnel, diluted with methylene chloride (500 ml), water (500 ml), and brine (500 ml). The aqueous layer was extracted four times with fresh methylene chloride (4 x 250 ml), and the combined organic layers were washed two times with fresh water and brine (2 x 500 ml), dried over magnesium sulfate, filtered, and evaporated to dryness under reduced pressure. The resulting residue was purified by flash chromatography, (SiO_2: gradient from 3:1 hexanes to ethyl acetate to 1:1 hexanes to ethyl acetate) to afford pure **18** (46.8 g, 80% yield) as a clear oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.81 (m, center, 1 H), 5.05-4.94 (m, 2 H), 3.75-3.72 (m, 2 H), 3.69-3.66 (m, 2 H), 3.64-3.61 (m, 2 H), 3.61-3.58 (m, 2 H), 3.48 (t, J = 6.7, 2 H), 2.42 (t, J = 6.1 Hz, 1H), 2.14-2.09 (m, 2 H), 1.70 (qt, J = 7.1, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.37, 115.02, 72.70, 70.99, 70.73, 70.43, 62.10, 30.41, 28.95. HRMS-EI (m/z): [M + H] calcd for $C_9H_{18}O_3$, 174.1256; found 174.1262.

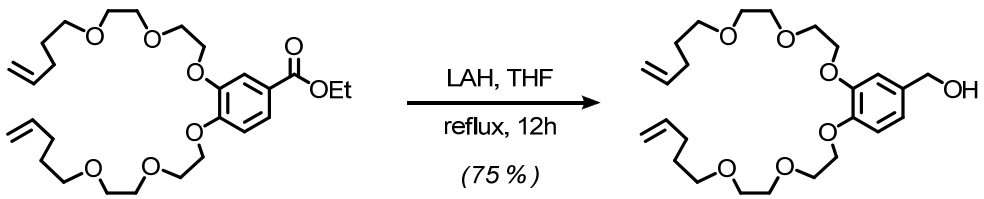


2-(2-(Pent-4-enyloxy)ethoxy)ethyl methanesulfonate (19). A cooled, flame-dried flask equipped with a stir bar and septum was charged with **18** (46.3 g, 0.266 moles, 1 eq) and dry DCM (300 ml, 0.9 M), then cooled to 0 °C. To the cooled reaction mixture was slowly added methanesulfonyl chloride (31 ml, 0.399 moles, 1.5 eq) and triethylamine (55.5 ml, 0.399 moles, 1.5 eq) alternately in several batches. The reaction was allowed to warm to room temperature and stirred overnight. Stirring was stopped and the reaction mixture poured into a separatory funnel and partitioned with water and brine (1 L). The aqueous layer was extracted three times with fresh DCM (3 x 300 ml), and the combined organic layers were washed three times with fresh water and brine (3 x 300 ml), dried over magnesium sulfate, filtered, and evaporated to dryness under reduced pressure. The resulting crude oil was purified by flash chromatography (plug of SiO_2: 3:2 hexanes to ethyl acetate) to give **19** (64.2 g, 96% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.80 ppm (m, 1 H), 5.04-4.94 (br m, 2 H), 4.39-4.37 (m, 2 H), 3.78-3.75 (m, 2 H), 3.67-3.64 (m, 2 H), 3.59-3.56 (m, 2 H), 3.45 (t, J = 6.6 Hz, 2 H), 3.06 (s, 1 H), 2.17-2.07 (m, 2 H), 1.67, (qt, J = 7.1 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 138.34, 115.01, 70.93, 70.92, 70.25, 69.48, 69.25, 37.92, 30.40, 28.97. HRMS-EI (m/z): [M + H] calcd for $C_{10}H_{21}O_5S$, 253.1110; found 253.1119.



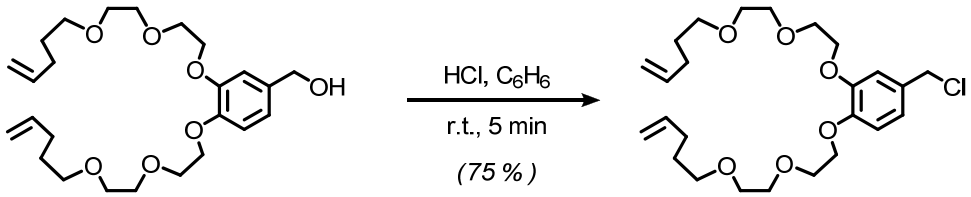
Ethyl Ester Crown-Type Recognition Fragment (21). Standard alkylation conditions were used with protocatechuic acid ethyl ester **20** (12.6345 g, 69.35 mmol, 1 eq), **19** (35.0000 g, 0.139 moles, 2 eq), K_2CO_3 (57.5217 g, 0.416 moles, 6 eq), and dry DMF (1

L, 0.07 M). After 3 days, the reaction was extracted and purified via flash chromatography (SiO_2: 4:1 hexanes to acetone), giving **21** (28.8 g, 84% yield) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (m, 1H), 7.53 (m, 1H), 6.86 (m, 1H), 5.75 (m, 2H), 5.05-4.84 (m, 4H), 4.28 (m, 2H), 4.16 (m, 4H), 3.84 (m, 4H), 3.68 (m, 4H), 3.54 (m, 4H), 3.41 (m, 4H), 2.13-1.98 (m, 4H), 1.62 (m, 4H), 1.31 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.36, 152.90, 148.28, 138.32, 138.30, 123.98, 123.39, 115.00, 114.81, 114.79, 112.69, 71.04, 70.97, 70.82, 70.28, 70.27, 69.71, 69.61, 68.91, 68.68, 60.84, 30.31, 28.85, 14.49. HRMS-TOF MS (m/z): [M + Na] calcd for $C_{27}H_{42}O_8Na$, 517.2777; found 517.2796.



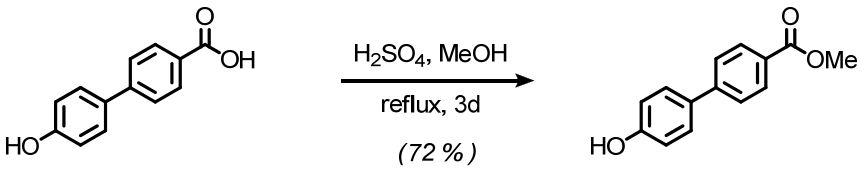
21 **22**

Benzyl Alcohol Crown-Type Recognition Fragment (22). Standard LAH reduction conditions were used with **21** (28.6 g, 63.24 mmol, 1 eq), LAH (7.1998 g, 0.190 moles, 3 eq), and dry THF (~630 ml, 0.1 M). The reaction was refluxed overnight, quenched, filtered, and extracted to give 2**2** (21.9 g, 75% yield) as a clear oil. The product was used with no further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (s, 1H), 6.87-6.79 (m, 2H), 5.79 (m, 2H), 5.04-4.85 (m 4H), 4.55 (s, 2H), 4.14 (m, 4H), 3.83 (t, J = 5.09 Hz, 4H), 3.60 (m, 4H), 3.57 (m, 4H), 3.45 (t, J = 6.60 Hz, 4H), 2.14 (s, 1H), 2.08 (q, J = 6.60 Hz, 4H), 1.66 (qt, J = 6.60 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.02, 148.33, 138.33, 134.74, 120.12, 114.83, 114.73, 113.75, 70.91, 70.85, 70.83, 70.25, 69.86, 69.83, 69.06, 68.84, 64.96, 30.31, 28.83. HRMS-TOF MS (m/z): [M + Na] calcd for $C_{25}H_{40}O_7Na$, 475.2672; found 475.2649.



22 **23**

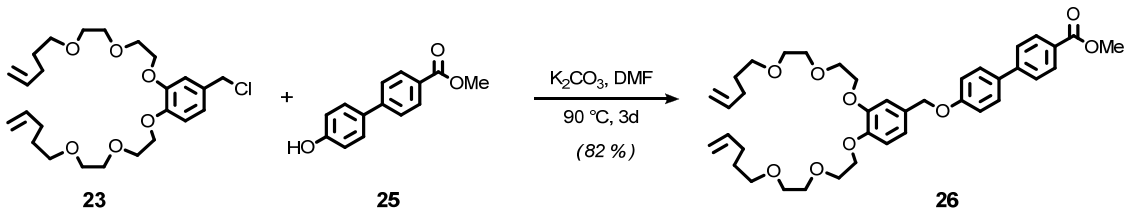
Benzyl Chloride Crown-Type Recognition Fragment (23). In a flask, **22** (21.9 g, 48.42 mmol, 1 eq) was dissolved in benzene (500 ml, 0.1 M), then transferred to a separatory funnel. To this mixture was added concentrated hydrochloric acid (241 ml). The reaction was shaken, with periodic venting, for 5 minutes. To quench the reaction, the solution was diluted with water (500 ml). The aqueous layer was extracted three times with fresh benzene (3 x 100 ml), and the combined organic layers were further washed with three portions of fresh water (3 x 100 ml), dried over magnesium sulfate, filtered, and evaporated to dryness under reduced pressure to provide **23** (21.4 g, 94% yield) as a pale yellow oil. The product was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96-6.78 (m, 3H), 5.78 (m, 2H), 5.05-4.89 (m, 4H), 4.49 (s, 2H), 4.14 (q, J = 5.14 Hz, 4H), 3.83 (m, 4H), 3.69 (m, 4H), 3.57 (m, 4H), 3.44 (m, 4H), 2.09 (q, J = 7.23 Hz, 4H), 1.66 (qt, J = 7.08 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.85, 148.69, 137.96, 130.40, 121.58, 114.83, 114.49, 114.00, 70.58, 70.38, 69.94, 69.45, 69.41, 68.69, 68.63, 46.18, 29.99, 28.55. HRMS-EI (m/z): [M + Na] calcd for $C_{25}H_{39}O_6NaCl$, 493.2333; found 493.2354.



24 **25**

Methyl Ester Backbone Fragment (25). A flask equipped with a stir bar was charged with 4'-hydroxy-4-biphenylcarboxylic acid **(24)** (9.1003 g, 42.48 mmol, 1 eq) and methanol (40 ml, 1 M). The solution was cooled to 0 °C, and concentrated sulfuric acid (6 ml, 33.2 mmol, 0.8 eq) was added dropwise. The flask was fitted with a reflux

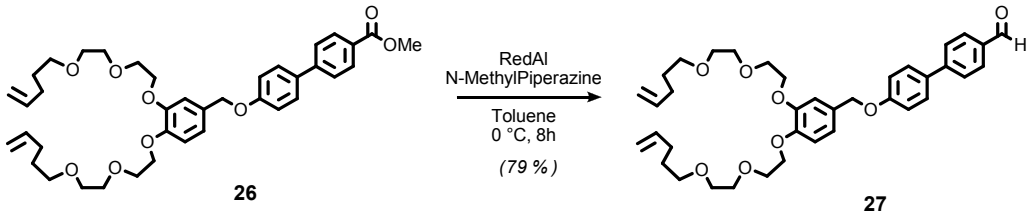
condenser, and the reaction heated to reflux for 5 hours. After cooling to 0 °C in an ice bath, a 10 % sodium hydroxide solution (150 ml) was added slowly to the reaction. The reaction mixture was poured into a separatory funnel, and diluted with ethyl acetate (250 ml) and water and brine (500 ml). The aqueous layer was extracted four times with ethyl acetate (4 x 100 ml), and the organic layers were combined, dried over magnesium sulfate, filtered, and evaporated to dryness under reduced pressure. Recrystallization from a minimum of hot ethyl acetate afforded **25** (7.0104 g, 72%) as a white crystalline solid. ^{1}H NMR (300 MHz, Acetone-d_6): δ 8.64 (s, 1H), 8.04 (d, J = 8.53 Hz, 2H), 7.73 (d, J = 8.80 Hz, 2H), 7.61 (d, J = 8.80 Hz, 2H), 6.97 (d, J = 8.80 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6): δ 167.22, 158.93, 146.31, 131.81, 130.83, 129.28, 129.08, 127.10, 116.84, 52.32. HRMS-FAB (m/z): [M + H] calcd for $C_{14}H_{12}O_3$, 228.0786; found 228.0796.



23 25 26

Methyl Ester Recognition-Backbone Fragment (26). Standard alkylation conditions were used with **23** (14.4292 g, 31.91 mmol, 1.05 eq), **25** (6.7775 g, 29.69 mmol, 1 eq), K_2CO_3 (12.3121 g, 89.07 mmol), and dry DMF (500 ml). The reaction was heated for 3 days, then extracted with ethyl acetate. The residue was purified via flash chromatography (SiO_2: gradient from 12:1 to 8:1 to 6:1 to 4:1 to 2:1 hexane to acetone) as eluent to give **26** (16.1 g, 82% yield) as a white crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 8.25 Hz, 2H), 7.60 (d, J = 8.25 Hz, 2H), 7.55 (d, J = 8.81 Hz, 2H), 7.03 (d, J = 8.80 Hz, 2H), 7.01-6.85 (m, 3H), 5.78 (m, 2H), 5.05-4.88 (m, 6H), 4.16 (m 4H), 3.91 (s, 3H), 3.85 (t, J = 5.09 Hz, 4H), 3.70 (m, 4H), 3.58 (m, 4H), 3.45 (m, 4H), 2.08 (m, 4H), 1.66 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.22, 159.16, 149.24, 149.00, 145.32, 138.43, 132.73, 130.26, 130.11, 128.52, 128.38, 126.63, 121.09, 115.46, 114.89, 114.77, 114.42, 71.04, 70.93, 70.36, 70.17, 69.90, 69.11, 69.07, 52.26, 30.41,

28.94. HRMS-TOF MS (m/z): [M + Na] calcd for $C_{39}H_{50}O_9Na$, 685.3353; found 685.3358.



26 **27**

Aldehyde Recognition-Backbone Fragment (27). A cooled, flame-dried two-neck flask equipped with a stir bar, water condenser, gas port, and septum was charged, under argon at 0 °C, with RedAl (9.84 ml, 32.79 mmol, 1 eq) and dry toluene (16.4 ml). To this stirring mixture was added, slowly, N-methylpiperazine (4.01 ml, 36.07 mmol, 1.2), and the reaction allowed to stir for 30 minutes at 0 °C. A separate cooled, flame-dried two-neck flask equipped with a stir bar, water condenser, gas port, and septum was charged, under argon at 0 °C, with **26** (16.1 g, 24.29 mmol) and dry toluene (25 ml). After the 30 minute incubation time, the RedAl solution was added dropwise to the stirring solution of **26** in toluene. The reaction was allowed to stir for 8 hours at 0 °C, then quenched by addition of water (20 ml). The reaction was poured into a separatory funnel, and partitioned between ethyl acetate (100 ml) and water (200 ml) and brine (200 ml). The aqueous layer was extracted two times with DCM (2 x 100 ml), and the ethyl acetate and DCM layers were combined and washed with fresh water and brine (2 x 200 ml), dried with magnesium sulfate, filtered, and the solvent removed under reduced pressure. Flash chromatography (SiO_2: 4:1 hexane to acetone) gave **27** (12.1 g, 79% yield) as a white crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.82 (d, J = 8.25 Hz, 2H), 7.61 (d, J = 8.26 Hz, 2H), 7.49 (d, J = 8.80 Hz, 2H), 6.98 (d, J = 8.57 Hz, 2H), 6.95-6.79 (m, 3H), 5.73 (m, 2H), 5.05-4.88 (m, 6H), 4.12 (q, J = 5.04 Hz, 4H), 3.81 (t, J = 4.95 Hz, 4H), 3.67 (t, J = 4.68, 4H), 3.53 (t, J = 4.68 Hz, 4H), 3.40 (m, 4H), 2.12-1.98 (m, 4H), 1.62 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.04, 159.42, 149.27, 149.05, 146.87, 138.41, 134.81, 132.37, 130.46, 130.01, 128.64, 127.20, 121.09, 115.55, 114.88, 114.81, 114.47, 71.03, 70.91, 70.35, 70.17, 69.89, 69.13, 69.10, 30.39, 28.93. HRMS-FAB (m/z): [M + H – H_2] calcd for $C_{38}H_{47}O_8$, 631.3271; found 631.3258.

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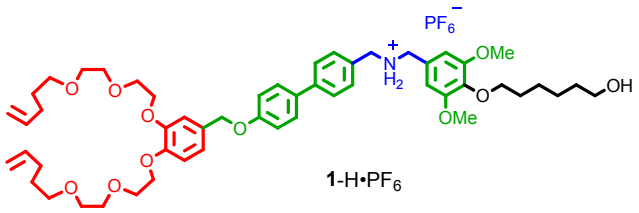

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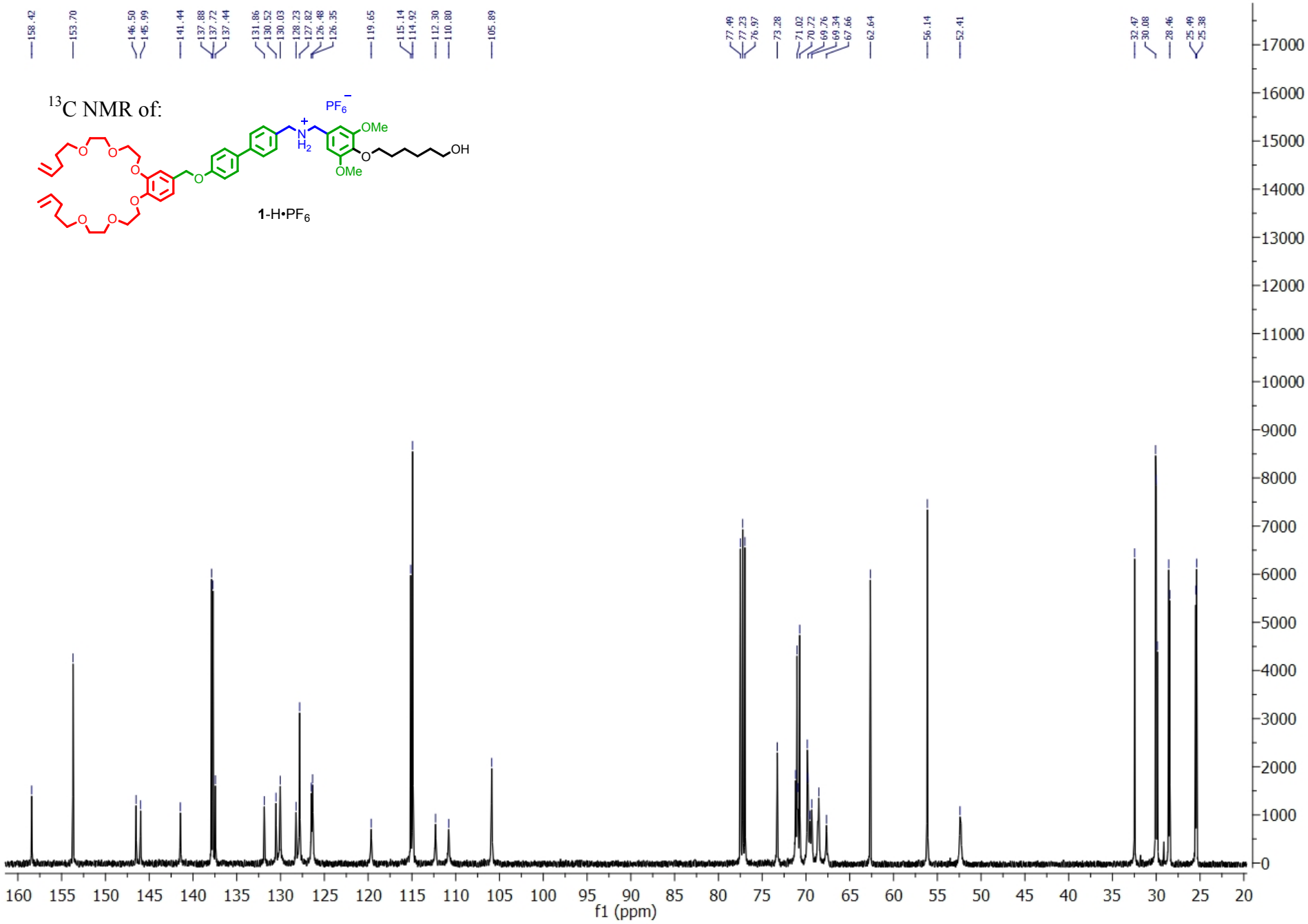
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f1 (ppm)

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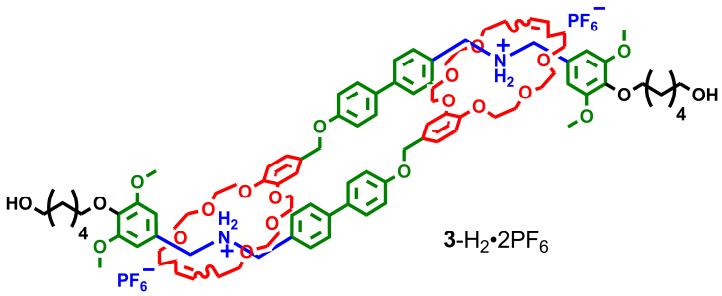

3-H_2•2PF_6

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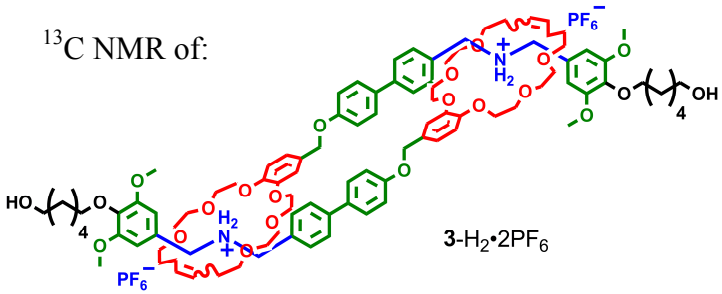

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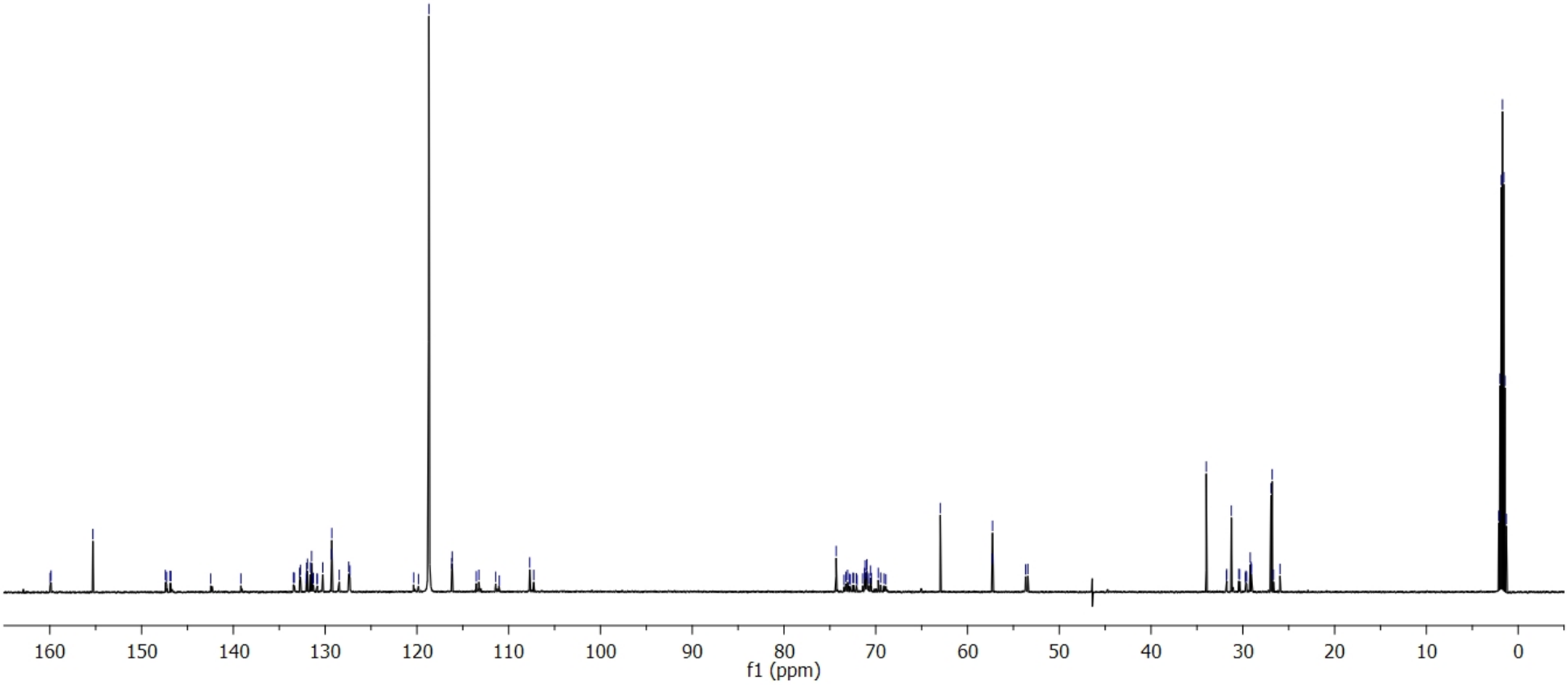

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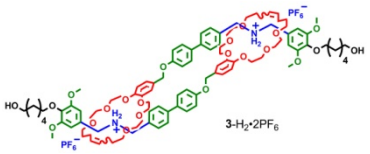
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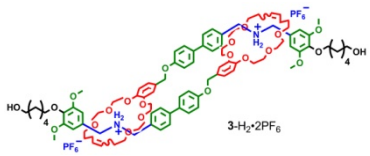

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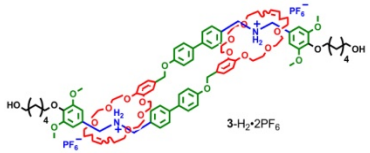

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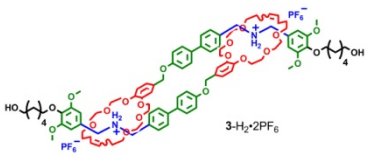
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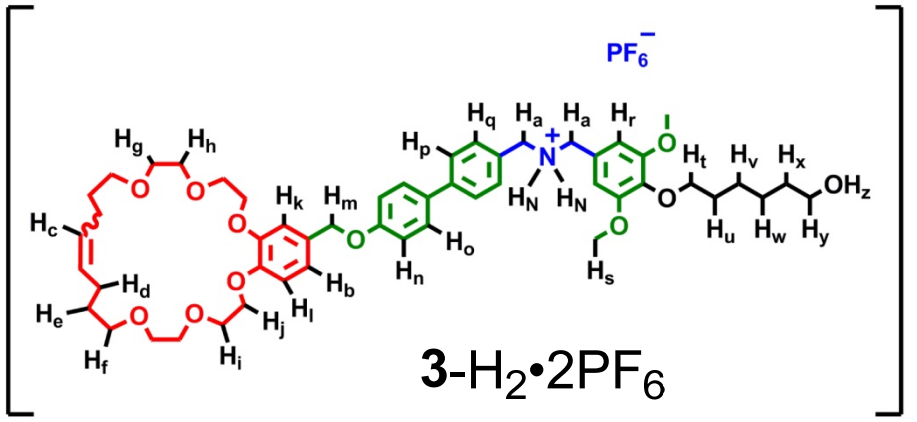

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$H_{b\,m}$ = H_k *meso*
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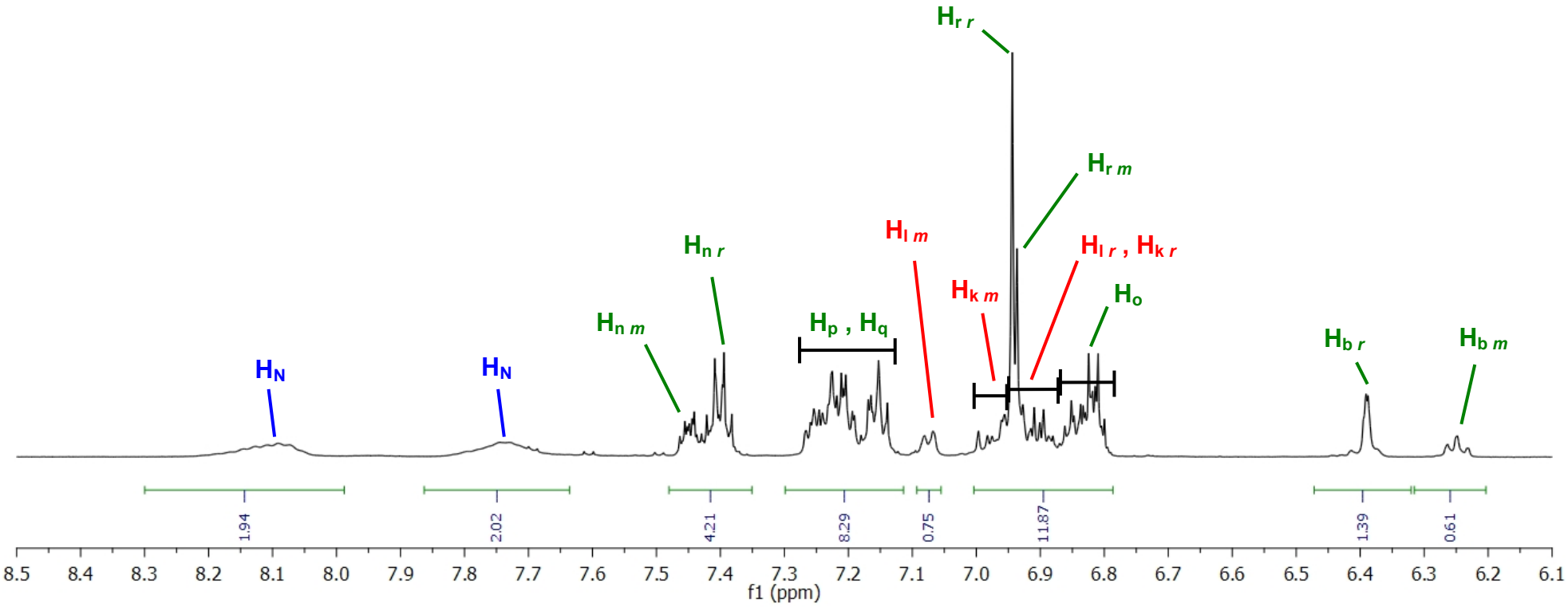

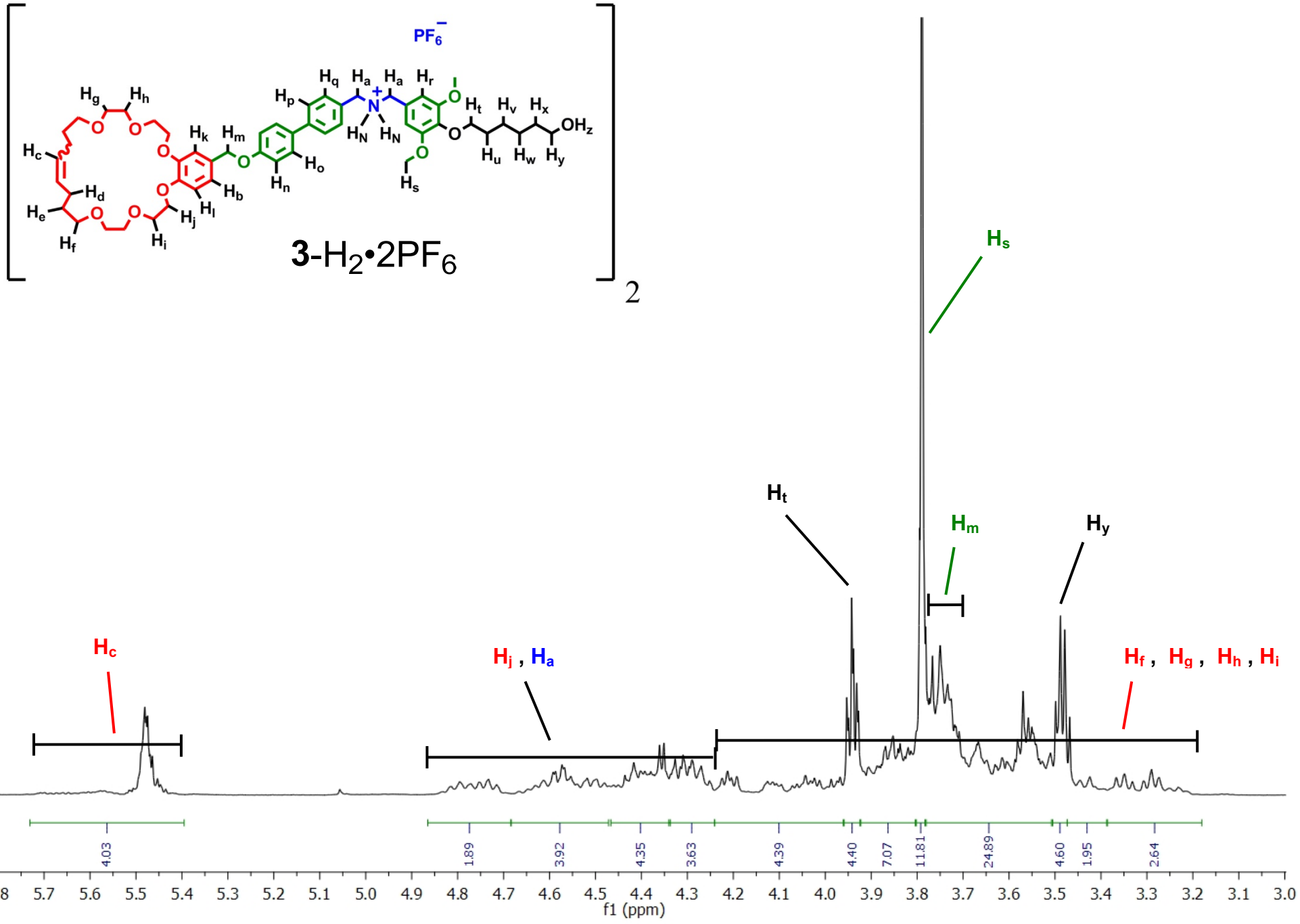
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Hm
Hy
Hc
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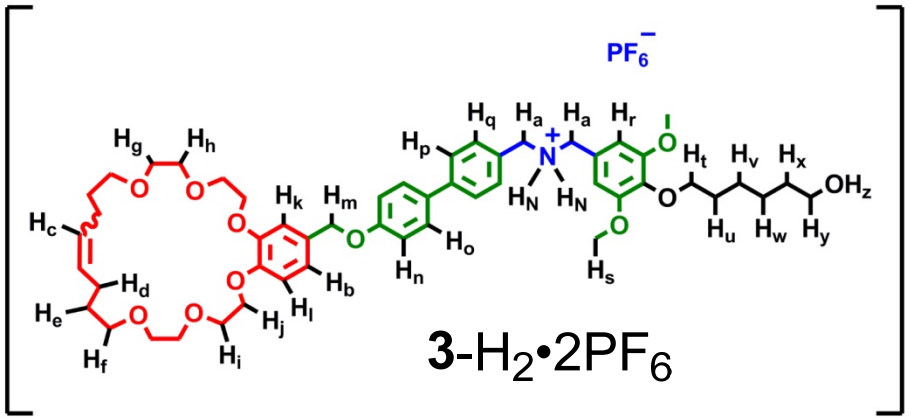
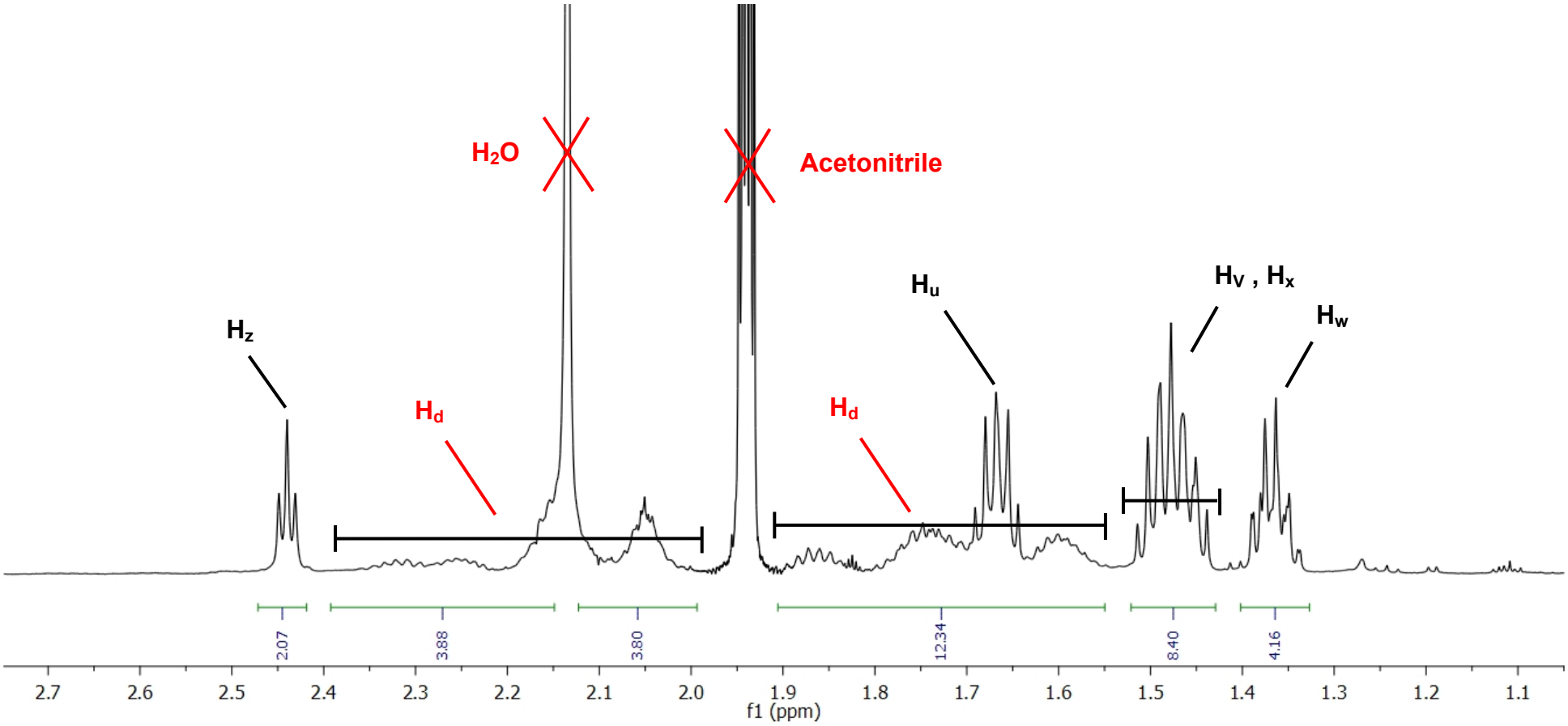
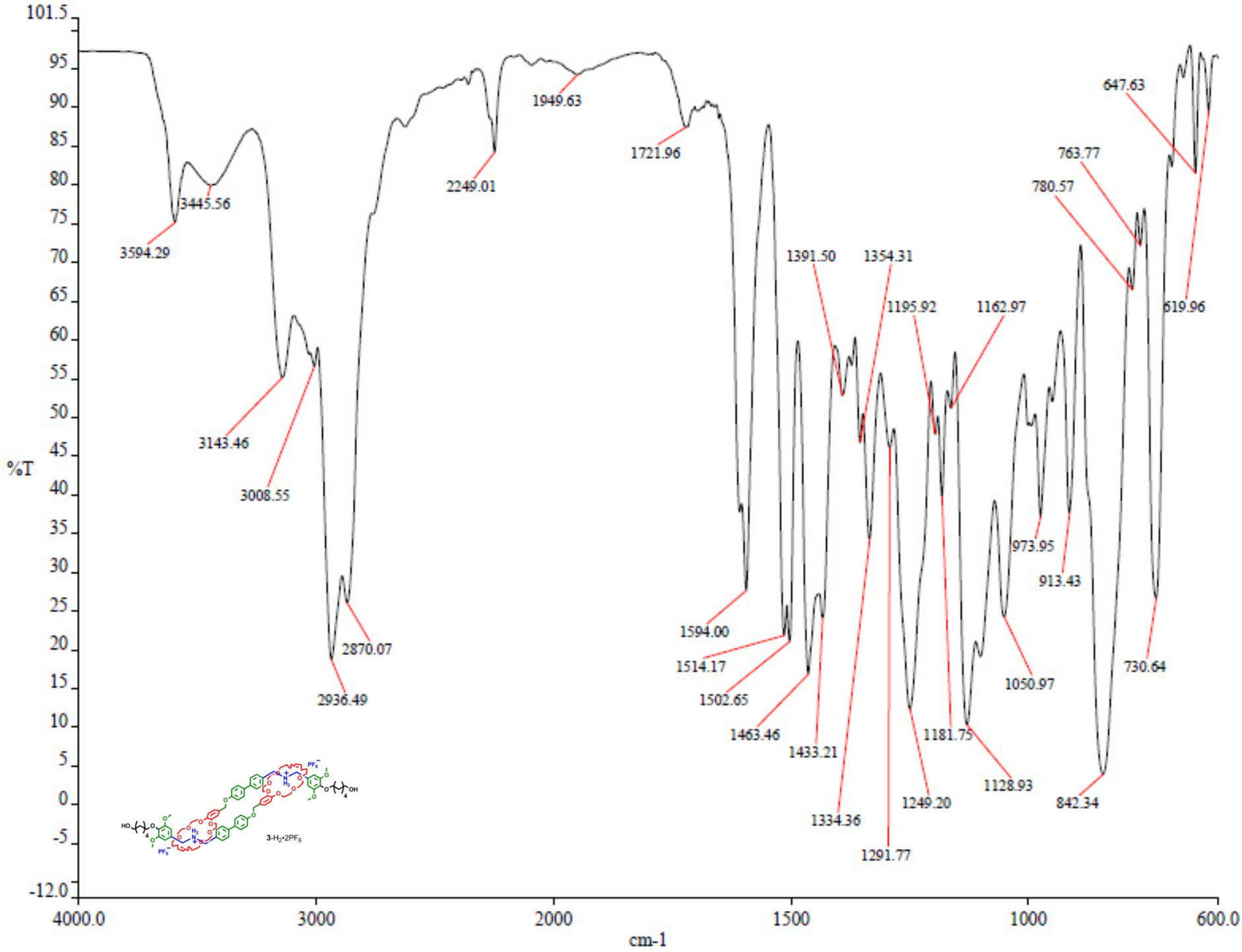
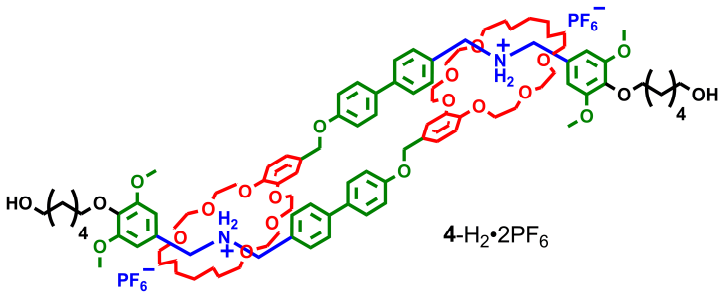
5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
f1 (ppm)


PF6−
Hg
Hh
Hc
Hk
Hm
Hq
Ha
Ha
Hr
Hp
HN
HN
N+
Ht
Hv
Hx
OHz
Hu
Hw
Hy
Hd
He
Hb
Hl
Hj
Hf
Hi
Ho
Hn
Hs
3-H2•2PF6
2


H2O
Acetonitrile
Hz
Hd
Hd
Hu
HV , Hx
Hw
2.07
3.88
3.80
12.34
8.40
4.16
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
f1 (ppm)

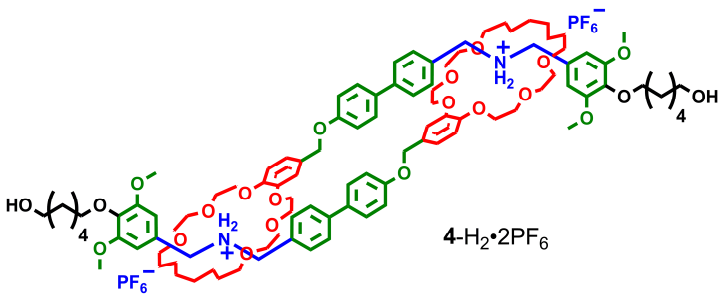

101.5
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-12.0
%T
4000.0
3000
2000
1500
1000
600.0
cm-1
3594.29
3445.56
3143.46
3008.55
2870.07
2936.49
2249.01
1949.63
1721.96
1594.00
1514.17
1502.65
1463.46
1433.21
1391.50
1354.31
1334.36
1291.77
1249.20
1195.92
1181.75
1162.97
1128.93
1050.97
973.95
913.43
842.34
763.77
780.57
730.64
647.63
619.96
3-H2•2PF6

^{1}H NMR of:

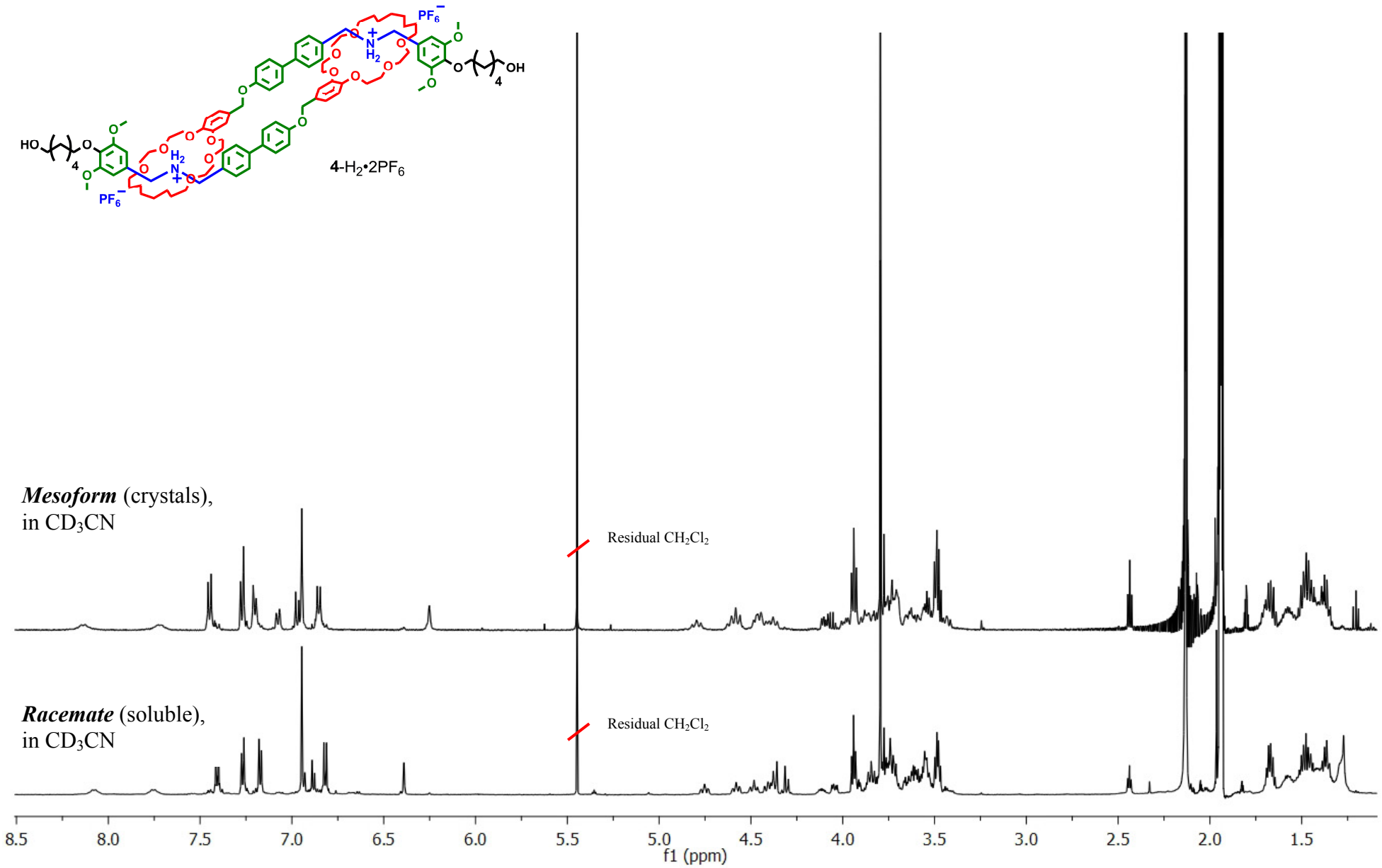


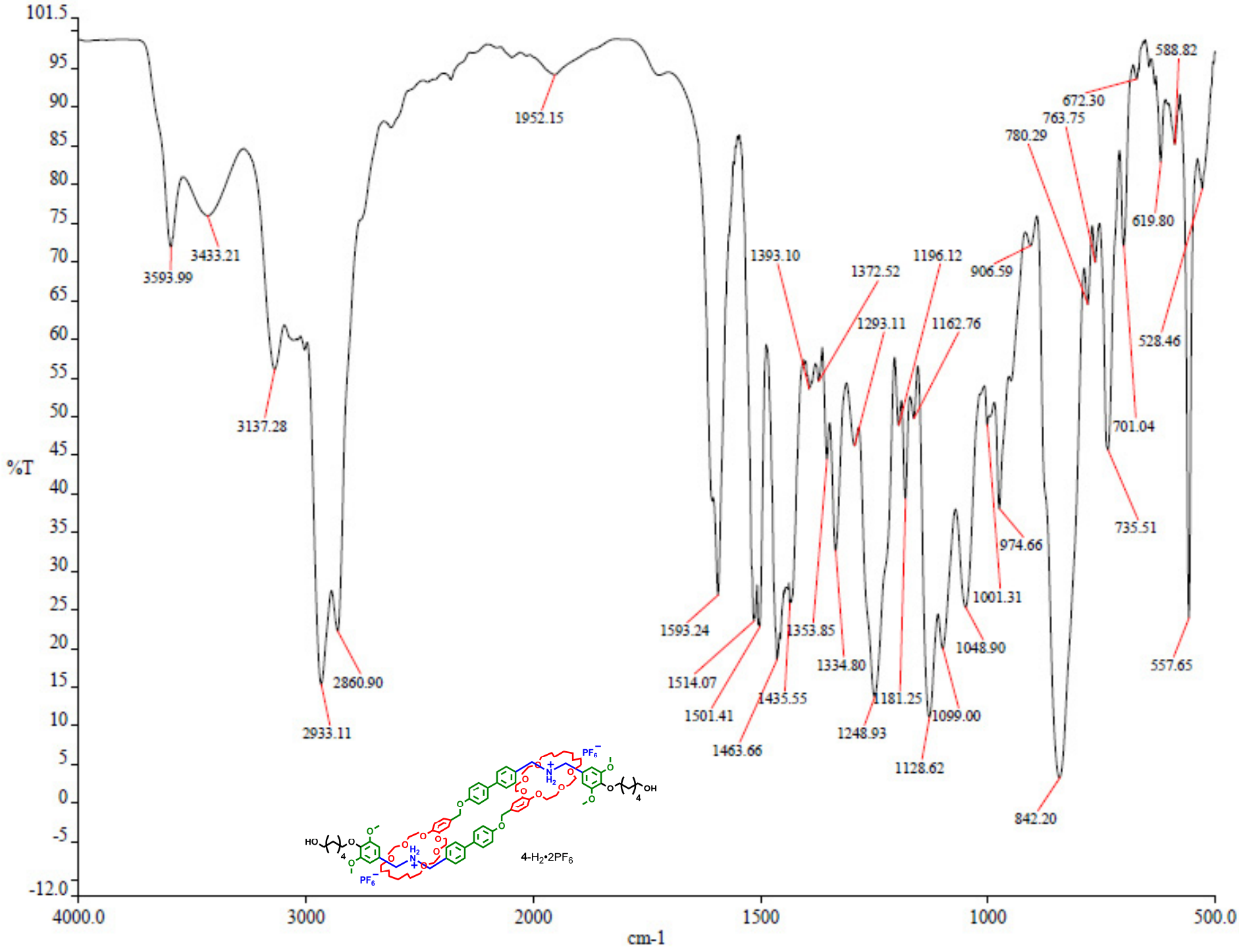
4-H_2•2PF_6

^{13}C NMR of:

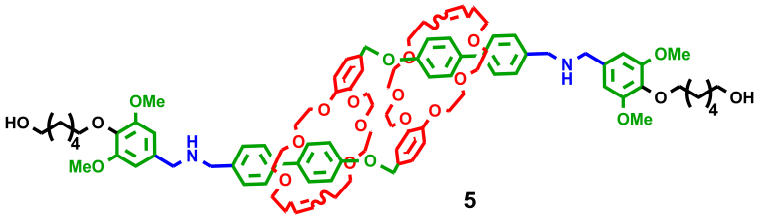


4-H_2•2PF_6


4-H2•2PF6
Mesoform (crystals), in CD3CN
Residual CH2Cl2
Racemate (soluble), in CD3CN
Residual CH2Cl2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


101.5
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-12.0
%T
4000.0
3000
2000
1500
1000
500.0
cm-1
3593.99
3433.21
3137.28
2933.11
2860.90
1952.15
1593.24
1514.07
1501.41
1463.66
1435.55
1393.10
1372.52
1353.85
1334.80
1293.11
1248.93
1196.12
1181.25
1162.76
1128.62
1099.00
1048.90
1001.31
974.66
906.59
842.20
780.29
763.75
735.51
701.04
672.30
619.80
588.82
557.65
528.46
4-H2•2PF6

^{1}H NMR of:

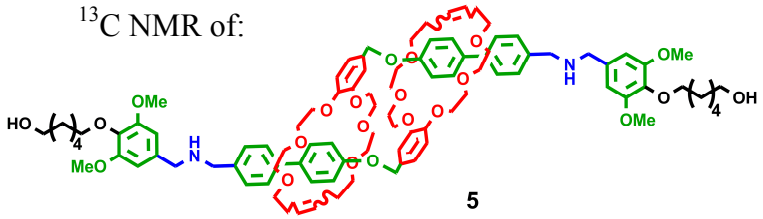

HO
OMe
MeO
H
N
OMe
OMe
N
H
O
OH

5

5.38
4.30
16.82
4.00
74.61
8.22
12.49
8.06
4.30
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

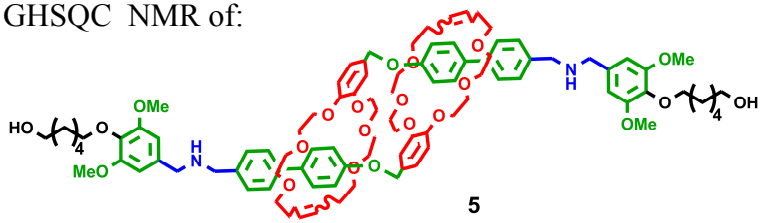
^{13}C NMR (126 MHz, cd$_3$cn) δ 159.48, 154.59, 148.98, 148.78, 147.07, 141.84, 140.98, 140.10, 139.12, 136.49, 134.58, 131.68, 131.10, 130.54, 130.02, 128.94, 126.69, 120.72, 118.69, 116.51, 116.18, 112.85, 107.55, 107.29, 74.05, 72.76, 71.85, 71.49, 71.04, 70.77, 70.60, 70.42, 70.01, 69.70, 69.03, 68.47, 62.72, 56.99, 56.89, 54.86, 53.48, 33.74, 31.73, 31.10, 30.40, 29.71, 27.68, 26.81, 26.66, 2.05, 1.88, 1.72, 1.55, 1.39, 1.22, 1.06.

^{13}C NMR of:



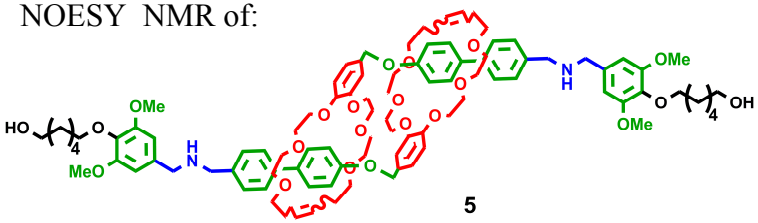
5

GHSQC NMR of:



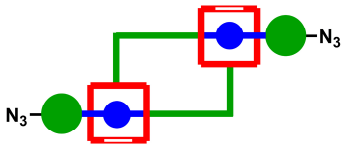
5

NOESY NMR of:

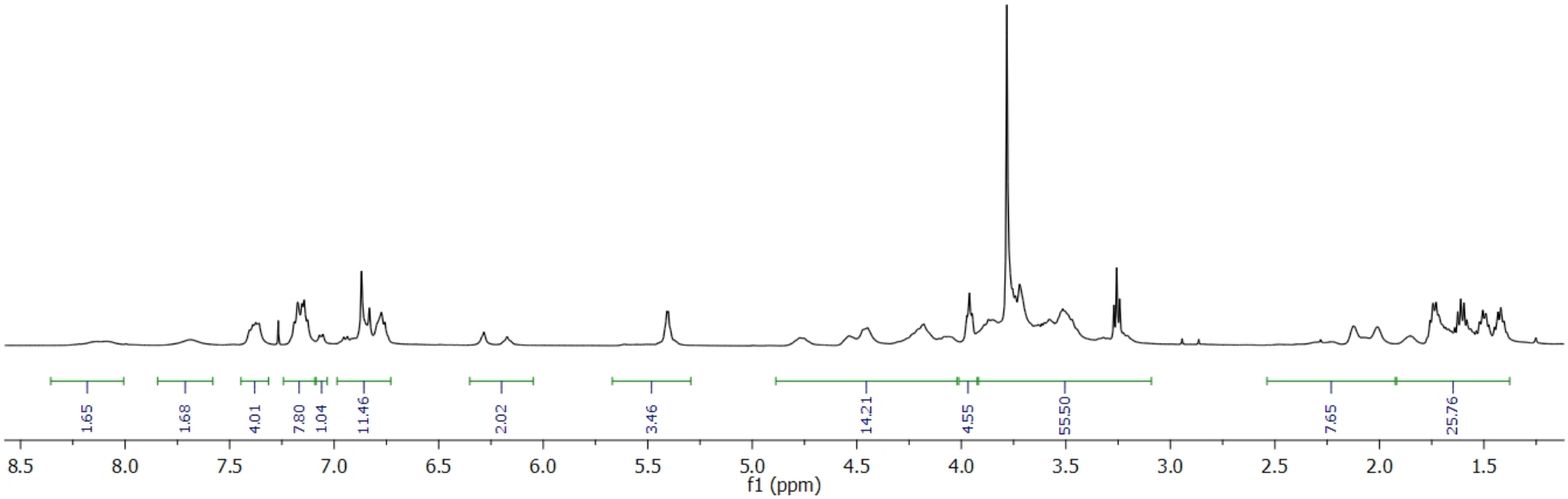


5

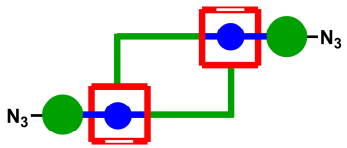
^{1}H NMR of:



6-H_2•2PF_6

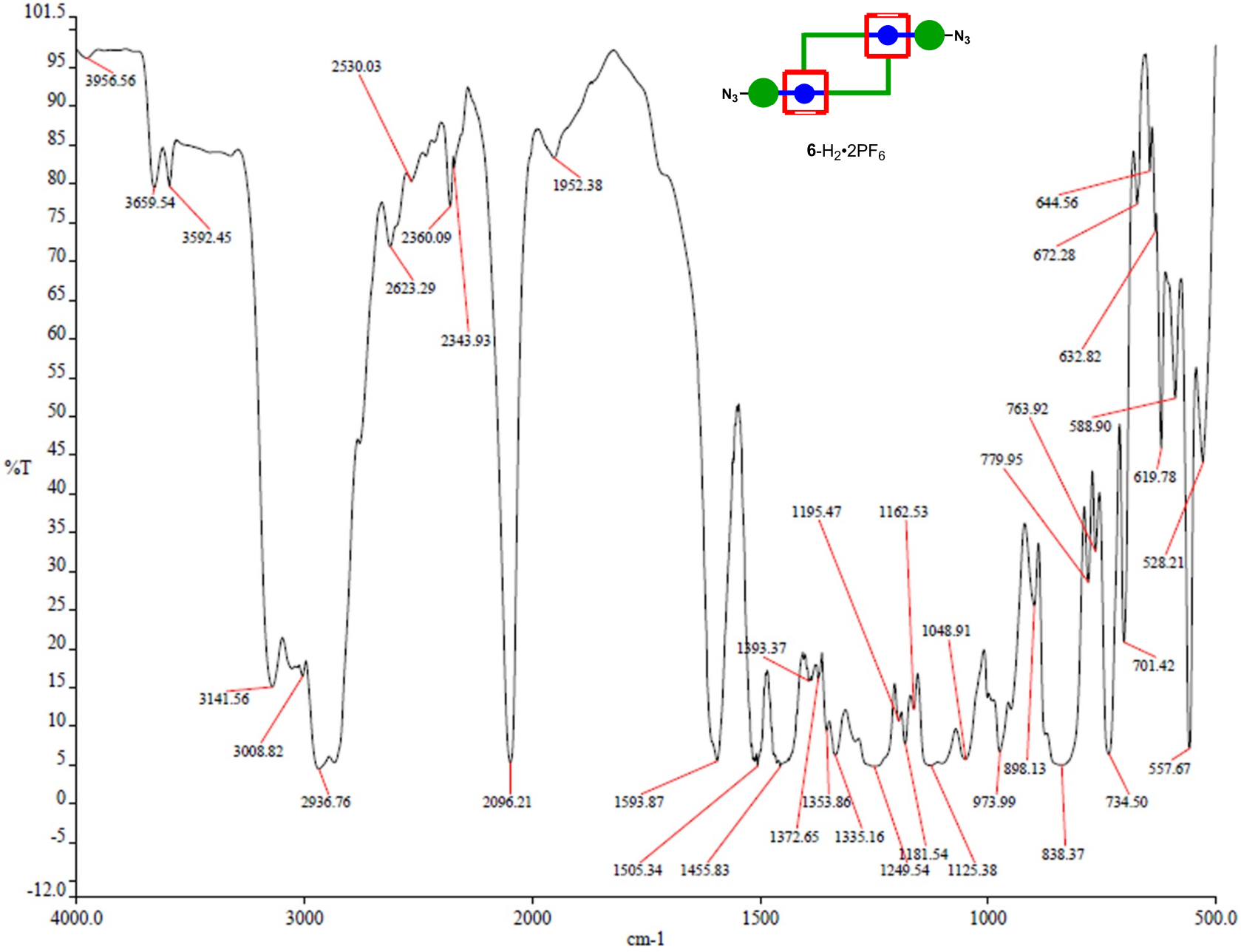


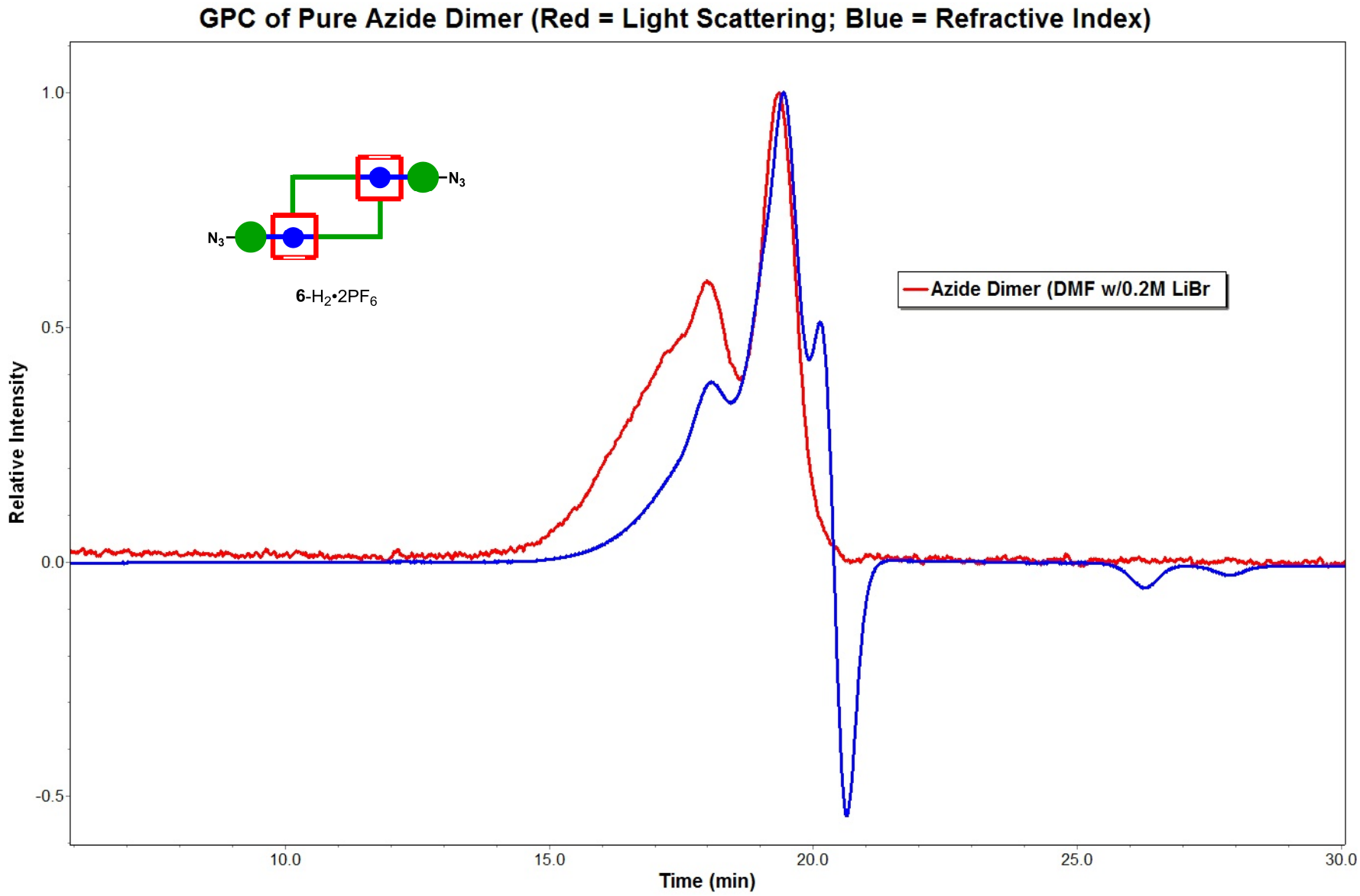
^{13}C NMR of:



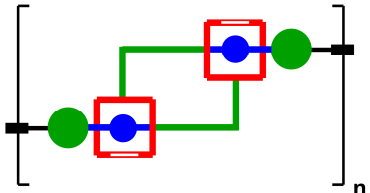
6-H_2•2PF_6

^{13}C NMR (126 MHz, cdcl$_3$) δ 158.54, 158.48, 154.06, 154.01, 145.86, 145.70, 145.31, 145.18, 141.53, 137.94, 131.62, 131.13, 130.61, 129.98, 128.24, 127.86, 127.13, 126.23, 119.28, 118.75, 114.97, 111.89, 111.75, 109.89, 109.57, 105.94, 105.30, 77.48, 77.23, 76.98, 73.57, 73.47, 72.36, 72.23, 71.99, 71.83, 71.36, 71.22, 71.16, 71.04, 70.36, 70.04, 69.88, 69.80, 69.40, 69.30, 68.67, 68.25, 67.93, 67.90, 67.57, 67.47, 62.89, 56.44, 56.40, 52.31, 52.27, 51.51, 32.79, 30.62, 30.54, 30.11, 30.05, 29.18, 29.14, 28.90, 28.39, 28.34, 28.15, 28.01, 26.59, 25.71, 25.62, 25.52, 24.96, 24.91.


101.5
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-12.0
%T
4000.0
3000
2000
1500
1000
500.0
cm-1
3956.56
3659.54
3592.45
2530.03
2360.09
2623.29
2343.93
1952.38
3141.56
3008.82
2936.76
2096.21
1593.87
1505.34
1455.83
1393.37
1372.65
1353.86
1335.16
1195.47
1181.54
1162.53
1249.54
1125.38
1048.91
973.99
898.13
838.37
779.95
763.92
734.50
701.42
644.56
672.28
632.82
619.78
588.90
557.67
528.21
N3
N3
6-H2•2PF6

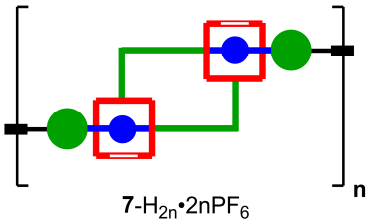

GPC of Pure Azide Dimer (Red = Light Scattering; Blue = Refractive Index)
1.0
0.5
0.0
-0.5
Relative Intensity
10.0
15.0
20.0
25.0
30.0
Time (min)
N3
N3
6-H2•2PF6
Azide Dimer (DMF w/0.2M LiBr

^{1}H NMR ($CDCl_3$) of:

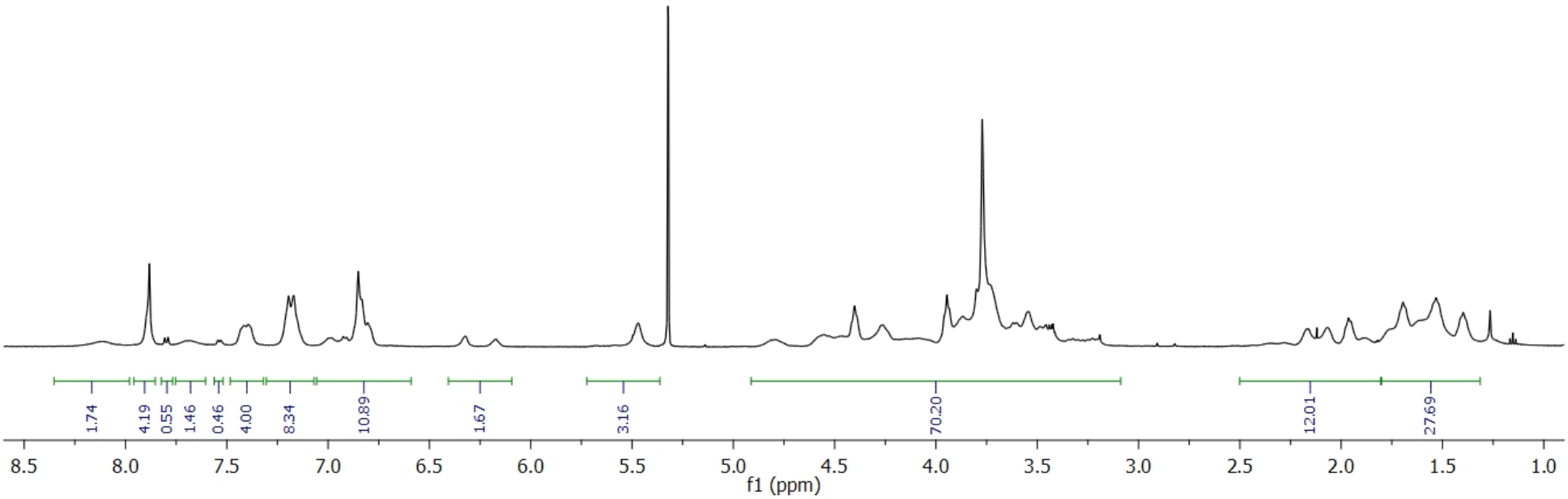


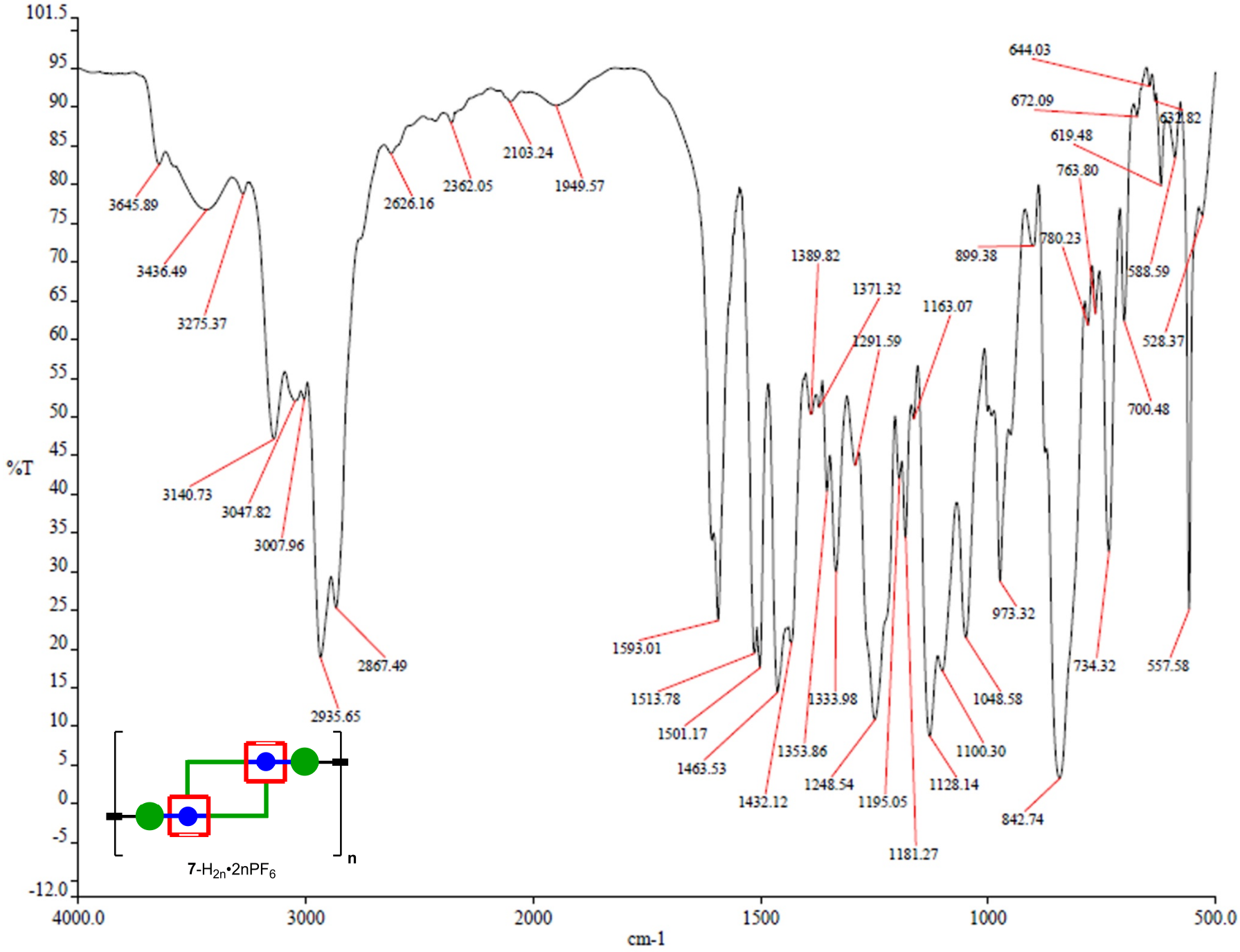
7-H_{2n}•2nPF_6

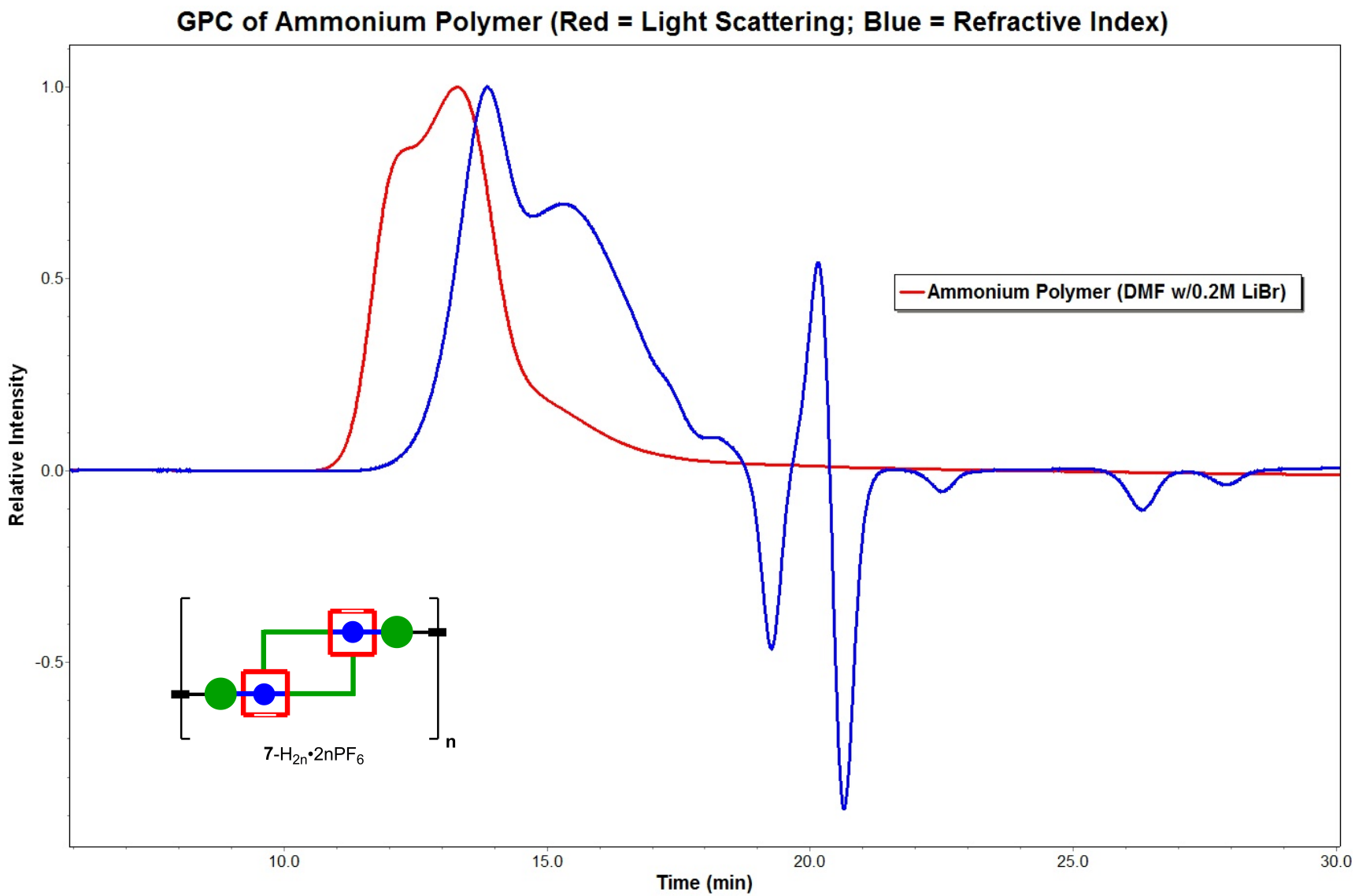
^{1}H NMR (CD_2Cl_2) of:



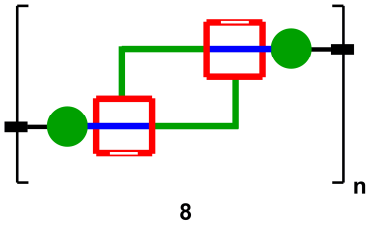
7-H_{2n}•2nPF_6



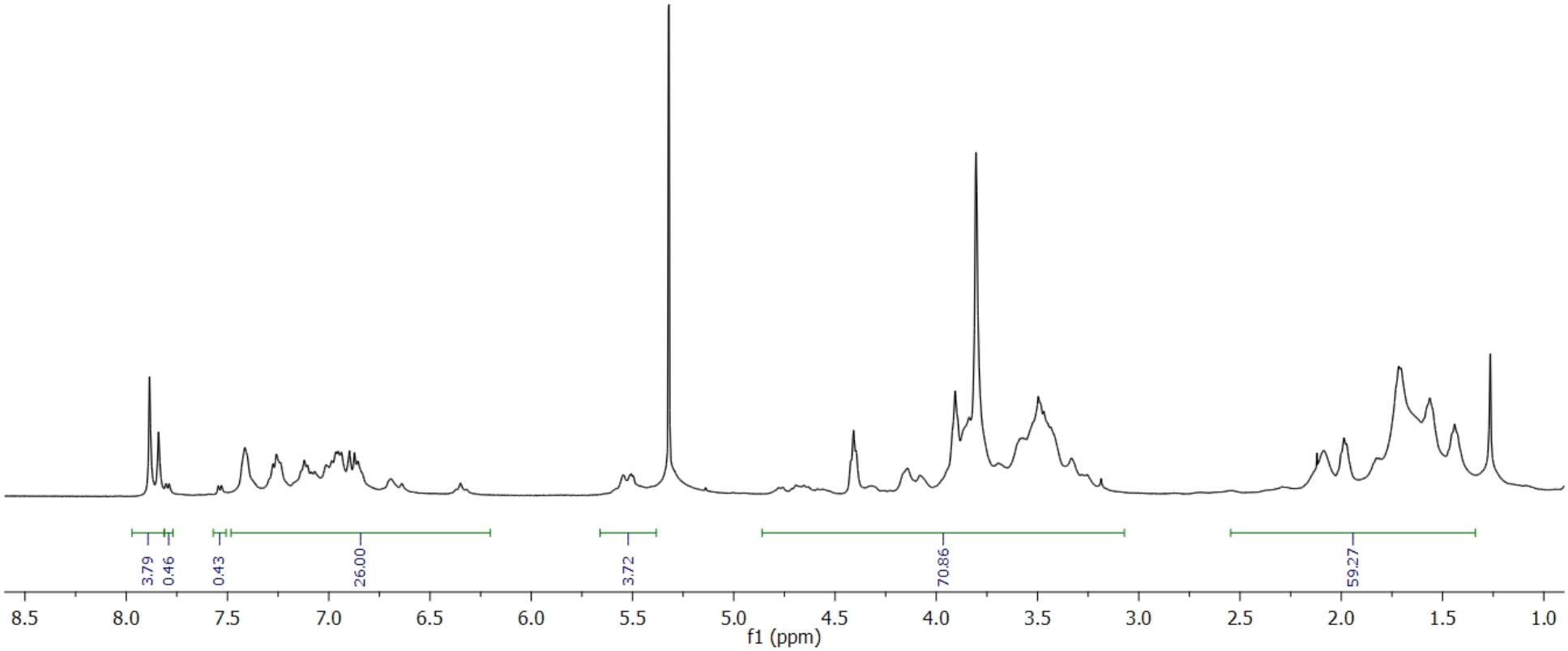

101.5
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-12.0
%T
4000.0
3000
2000
1500
1000
500.0
cm-1
3645.89
3436.49
3275.37
3140.73
3047.82
3007.96
2935.65
2867.49
2626.16
2362.05
2103.24
1949.57
1593.01
1513.78
1501.17
1463.53
1432.12
1389.82
1371.32
1353.86
1333.98
1291.59
1248.54
1195.05
1181.27
1163.07
1128.14
1100.30
1048.58
973.32
899.38
842.74
780.23
763.80
734.32
672.09
644.03
632.82
619.48
588.59
557.58
528.37
700.48
n
7-H2n•2nPF6


GPC of Ammonium Polymer (Red = Light Scattering; Blue = Refractive Index)
Relative Intensity
1.0
0.5
0.0
-0.5
10.0
15.0
20.0
25.0
30.0
Time (min)
Ammonium Polymer (DMF w/0.2M LiBr)
7-H2n•2nPF6
n

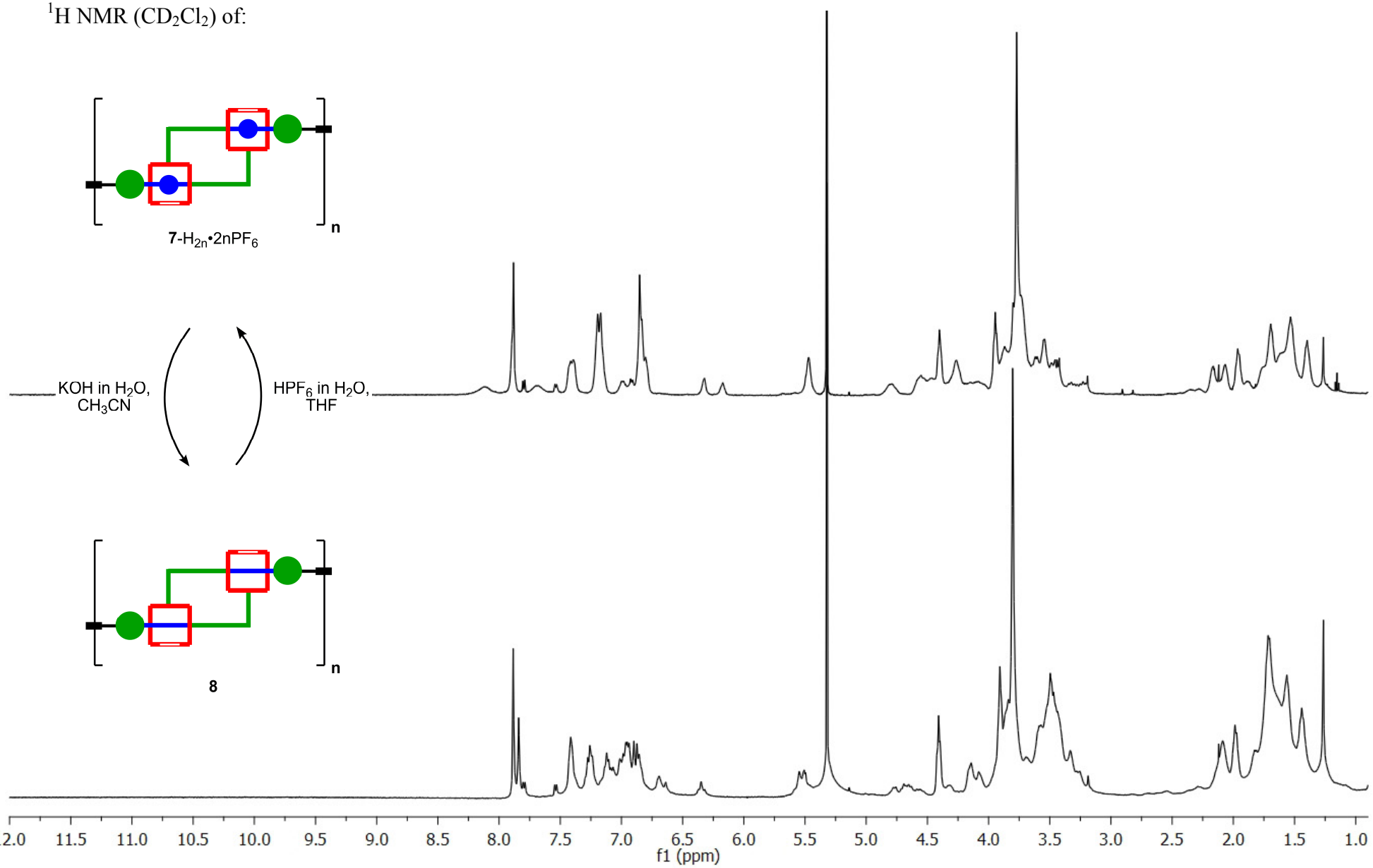
^{1}H NMR of:


n

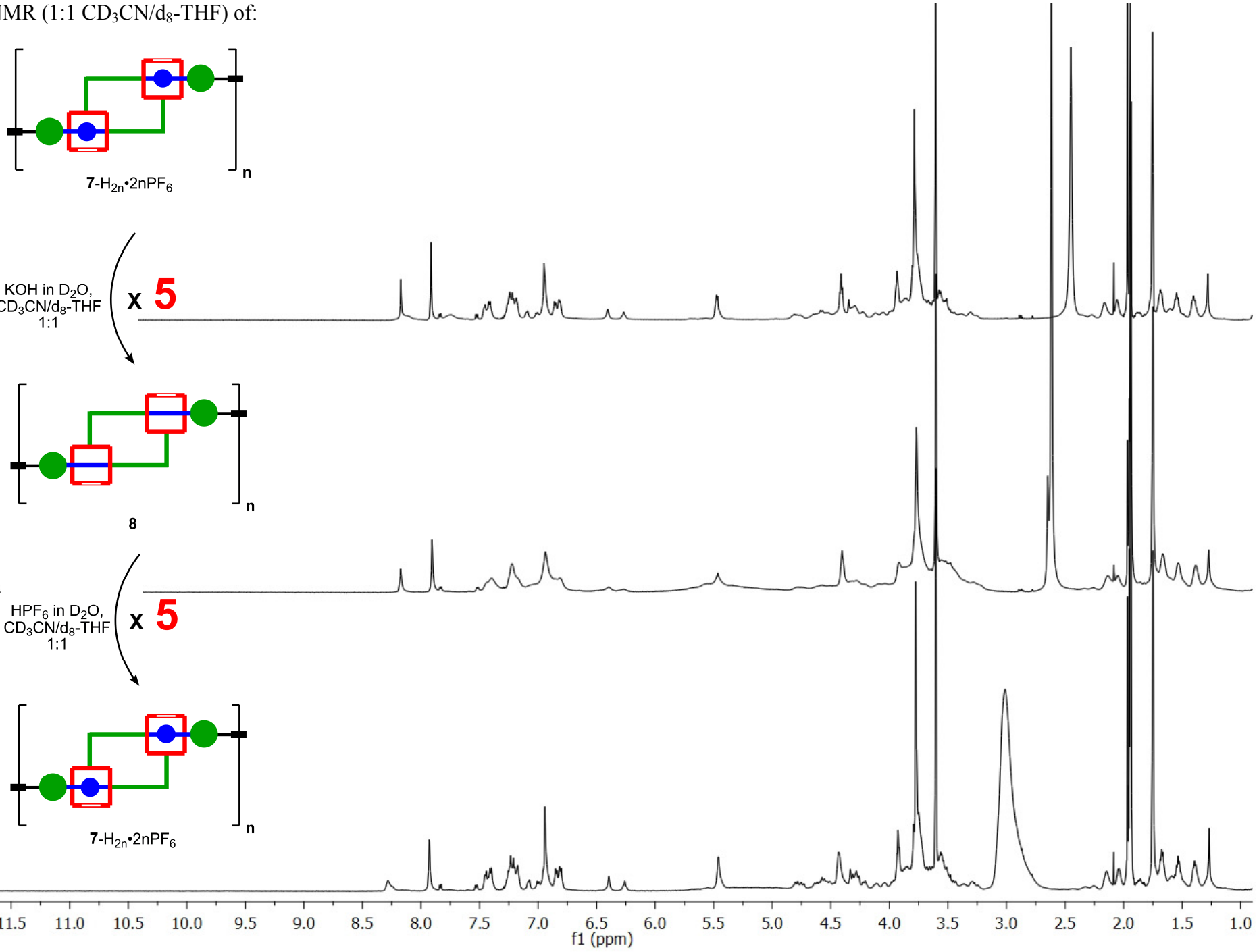
8

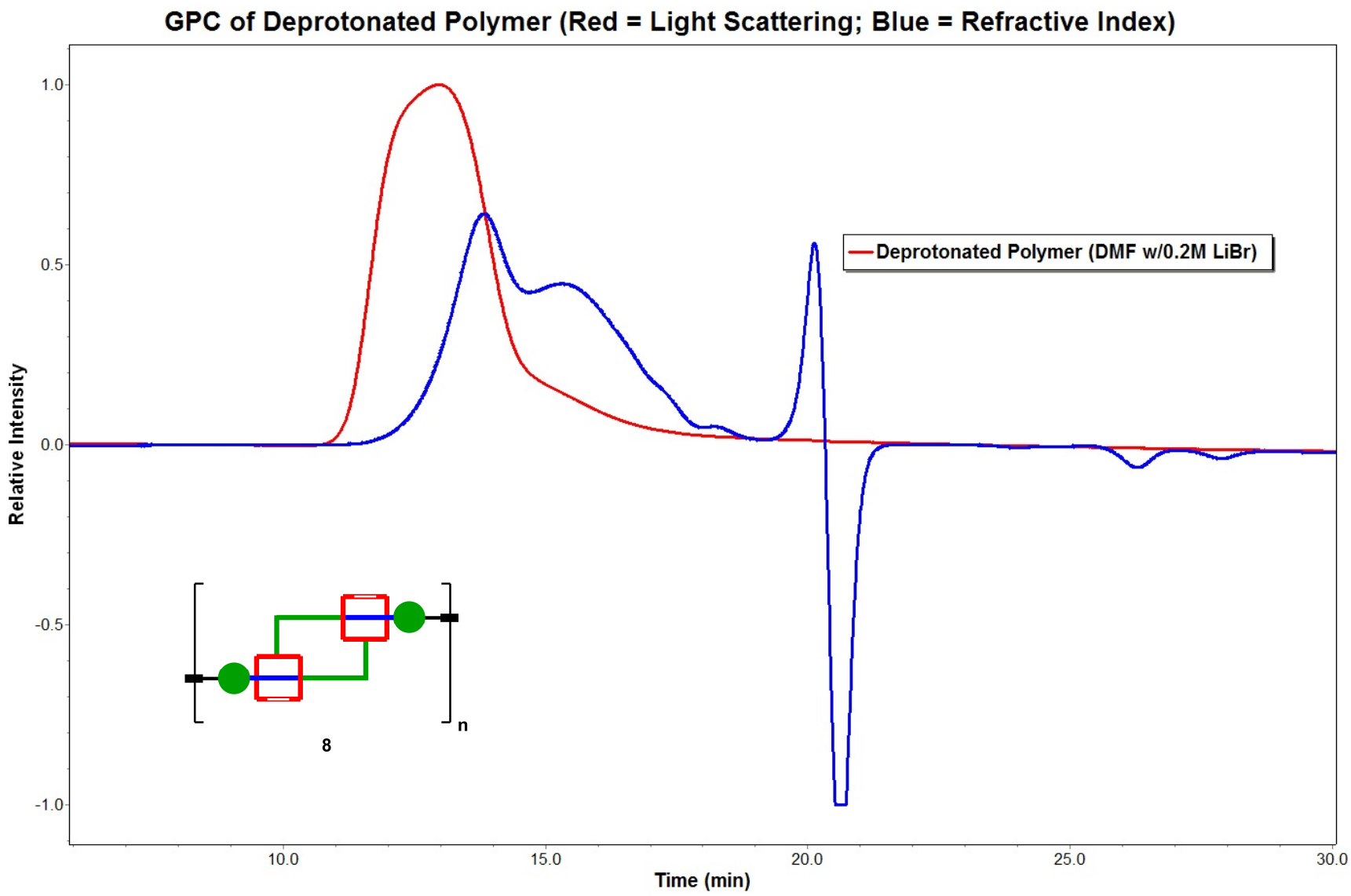

3.79
0.46
0.43
26.00
3.72
70.86
59.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

^{1}H NMR (CD_2Cl_2) of:

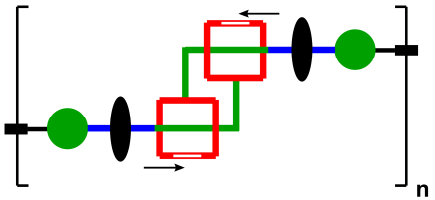


^{1}H NMR (1:1 CD_3CN/d_8-THF) of:

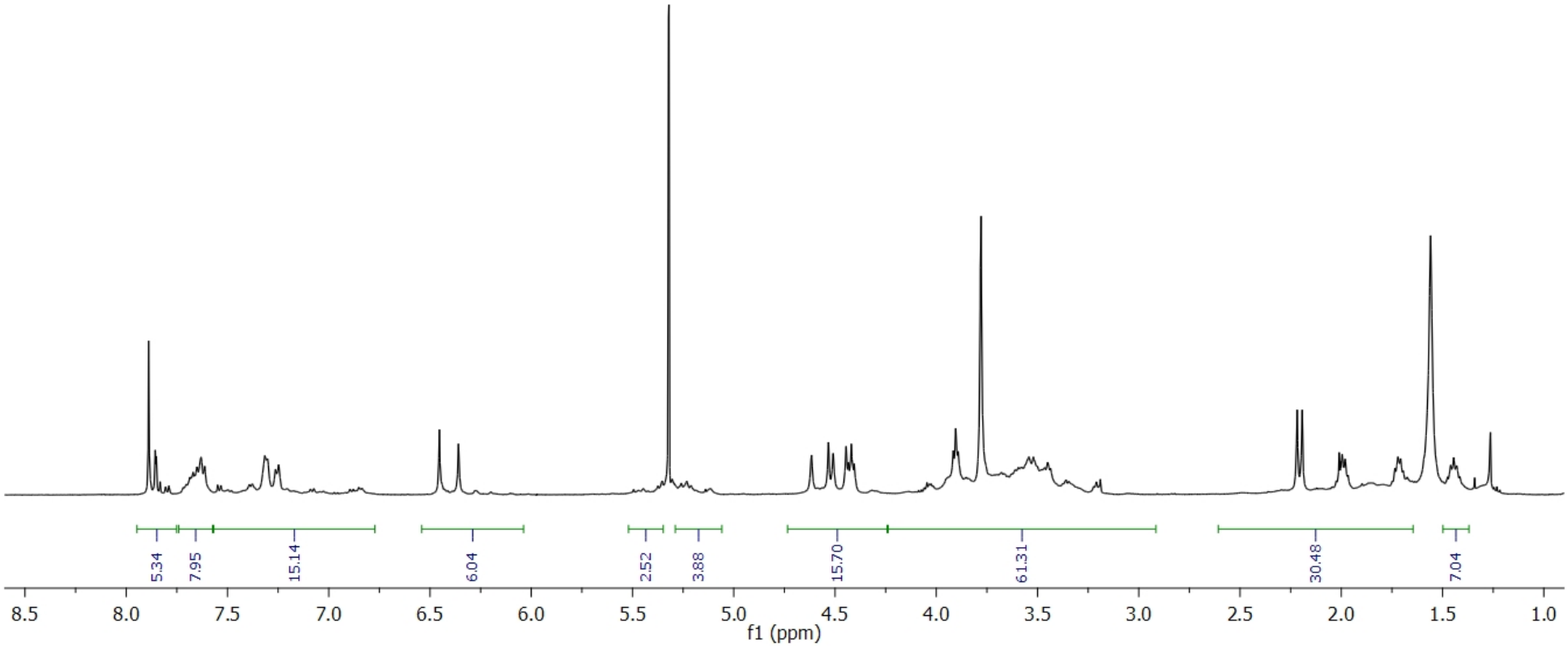


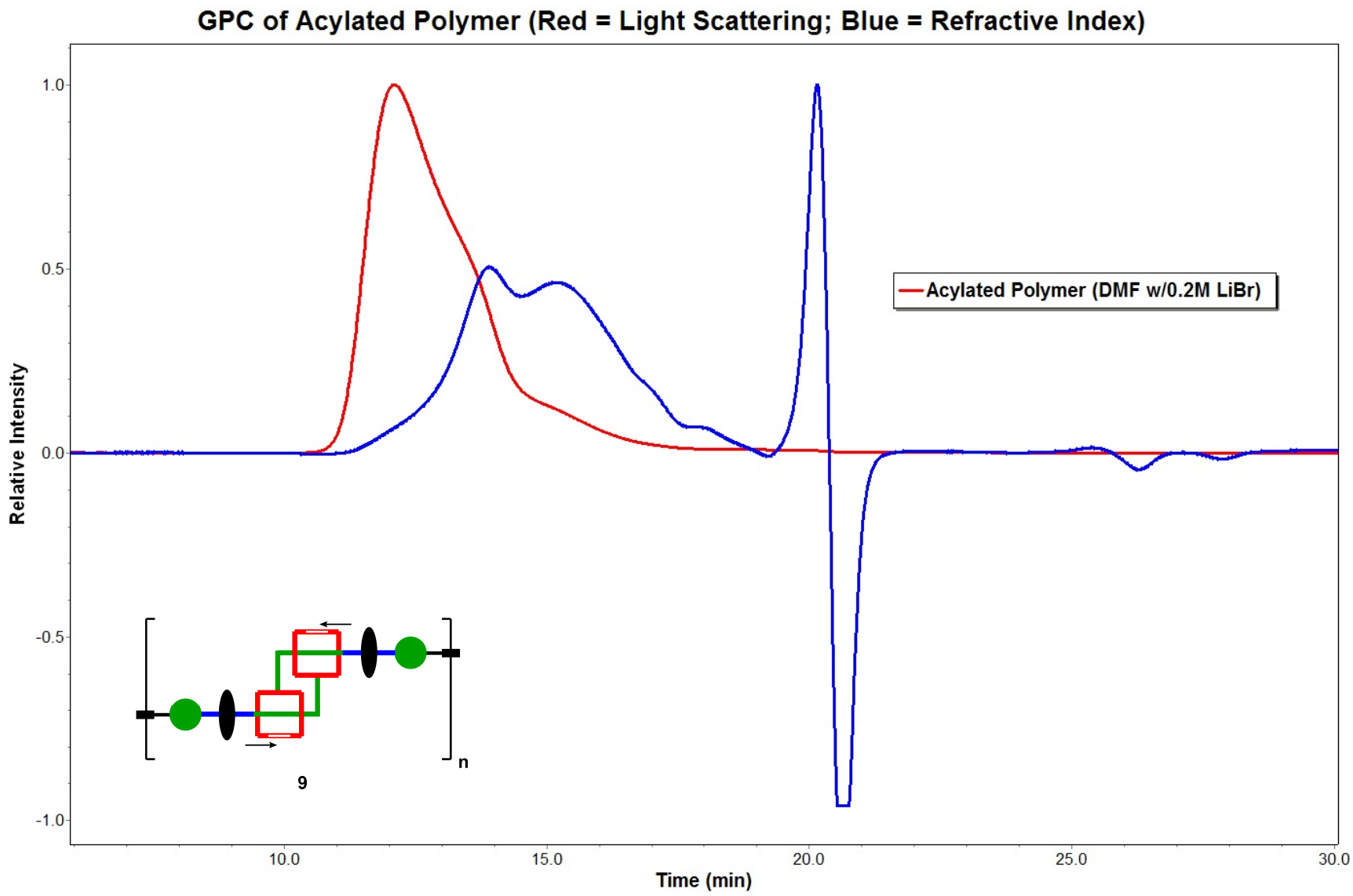

GPC of Deprotonated Polymer (Red = Light Scattering; Blue = Refractive Index)
Deprotonated Polymer (DMF w/0.2M LiBr)
Relative Intensity
1.0
0.5
0.0
-0.5
-1.0
10.0
15.0
20.0
25.0
30.0
Time (min)
8
n

^{1}H NMR of:

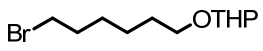

n

9


5.34
7.95
15.14
6.04
2.52
3.88
15.70
61.31
30.48
7.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

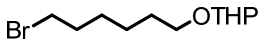

GPC of Acylated Polymer (Red = Light Scattering; Blue = Refractive Index)
Relative Intensity
1.0
0.5
0.0
-0.5
-1.0
10.0
15.0
20.0
25.0
30.0
Time (min)
Acylated Polymer (DMF w/0.2M LiBr)
9
n

^{1}H NMR of:



11

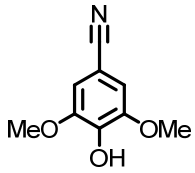
^{13}C NMR of:


Br
OTHP

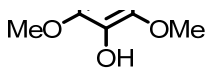
11

99.05
77.48
77.23
76.98
67.56
62.54
34.02
32.92
30.94
29.73
28.18
25.67
25.65
19.87
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of:

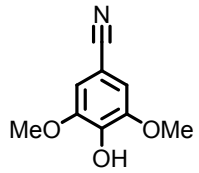


13



12

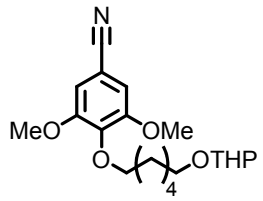
^{13}C NMR of:


N
MeO
OMe
OH

13

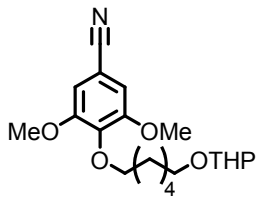
206.66
148.95
141.51
120.15
110.41
102.06
56.91
30.69
30.43
30.18
29.92
29.66
29.41
29.15
f1 (ppm)

^{1}H NMR of:



14

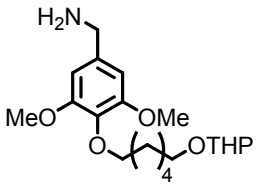
^{13}C NMR of:


N
MeO
OMe
O
OTHP
4

14

153.83
141.77
119.06
109.50
106.45
98.90
77.49
77.23
76.98
73.65
67.55
62.39
56.39
30.82
30.03
29.75
25.53
19.76
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

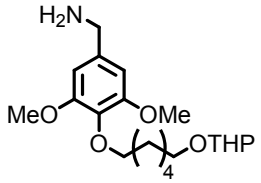
^{1}H NMR of:


H2N
MeO
OMe
O
OTHP
4

15

8E+05
8E+05
7E+05
6E+05
6E+05
6E+05
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
-50000
1.97
1.00
2.11
9.31
1.13
1.05
1.05
18.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

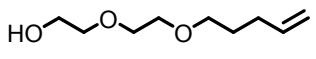
^{13}C NMR of:


H2N
MeO
OMe
O
OTHP
4

15

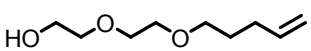
153.58
138.75
136.09
104.11
98.89
77.48
77.23
76.97
73.39
67.66
62.39
56.15
46.79
30.84
30.08
29.81
25.56
19.76
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of:



18

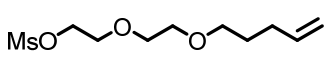
^{13}C NMR of:



18

138.37
115.02
77.48
77.23
76.98
72.70
70.99
70.73
70.43
62.10
30.41
28.95
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

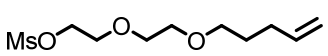
^{1}H NMR of:


MsO
O
O

19

20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0.75
1.60
1.87
1.88
1.95
1.96
1.97
3.00
1.84
1.90
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

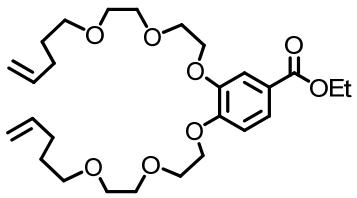
^{13}C NMR of:


MsO
O
O

19

138.34
115.01
77.48
77.23
76.98
70.93
70.92
70.25
69.48
69.25
37.92
30.40
28.97
f1 (ppm)

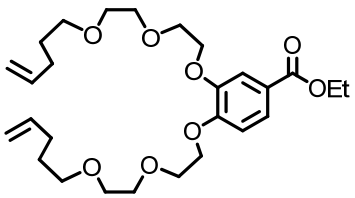
^{1}H NMR of:


O
OEt

21

5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.00
1.03
1.07
1.74
3.67
2.07
4.28
4.25
4.25
4.29
4.26
4.01
4.24
3.17
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

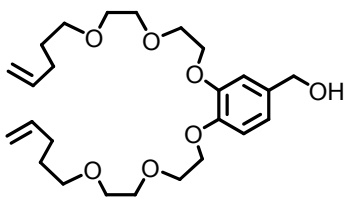
^{13}C NMR of:


O
O
O
O
O
O
O
OEt

21

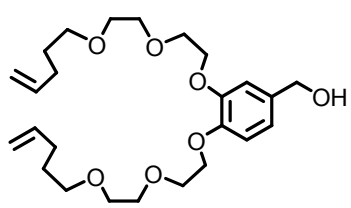
166.36
152.90
148.28
138.32
138.30
123.98
123.39
115.00
114.81
114.79
112.69
77.65
77.23
76.81
70.82
70.27
69.71
69.61
68.91
68.68
60.84
30.31
28.85
14.49
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR of:



22

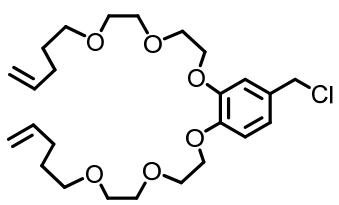
^{13}C NMR of:


OH

22

149.02
148.33
138.33
134.74
120.12
114.83
114.73
113.75
77.65
77.23
76.81
70.25
69.86
69.83
69.06
68.84
64.96
30.31
28.83
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

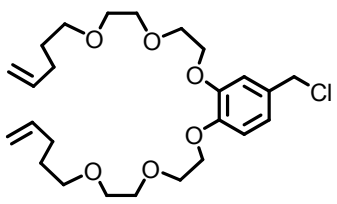
^{1}H NMR of:


O
O
O
O
O
O
Cl

23

21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
3.07
1.75
3.64
2.00
4.18
4.20
4.19
4.18
4.30
3.95
4.19
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

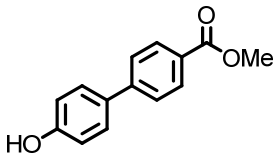
^{13}C NMR of:


O
O
O
O
O
O
Cl

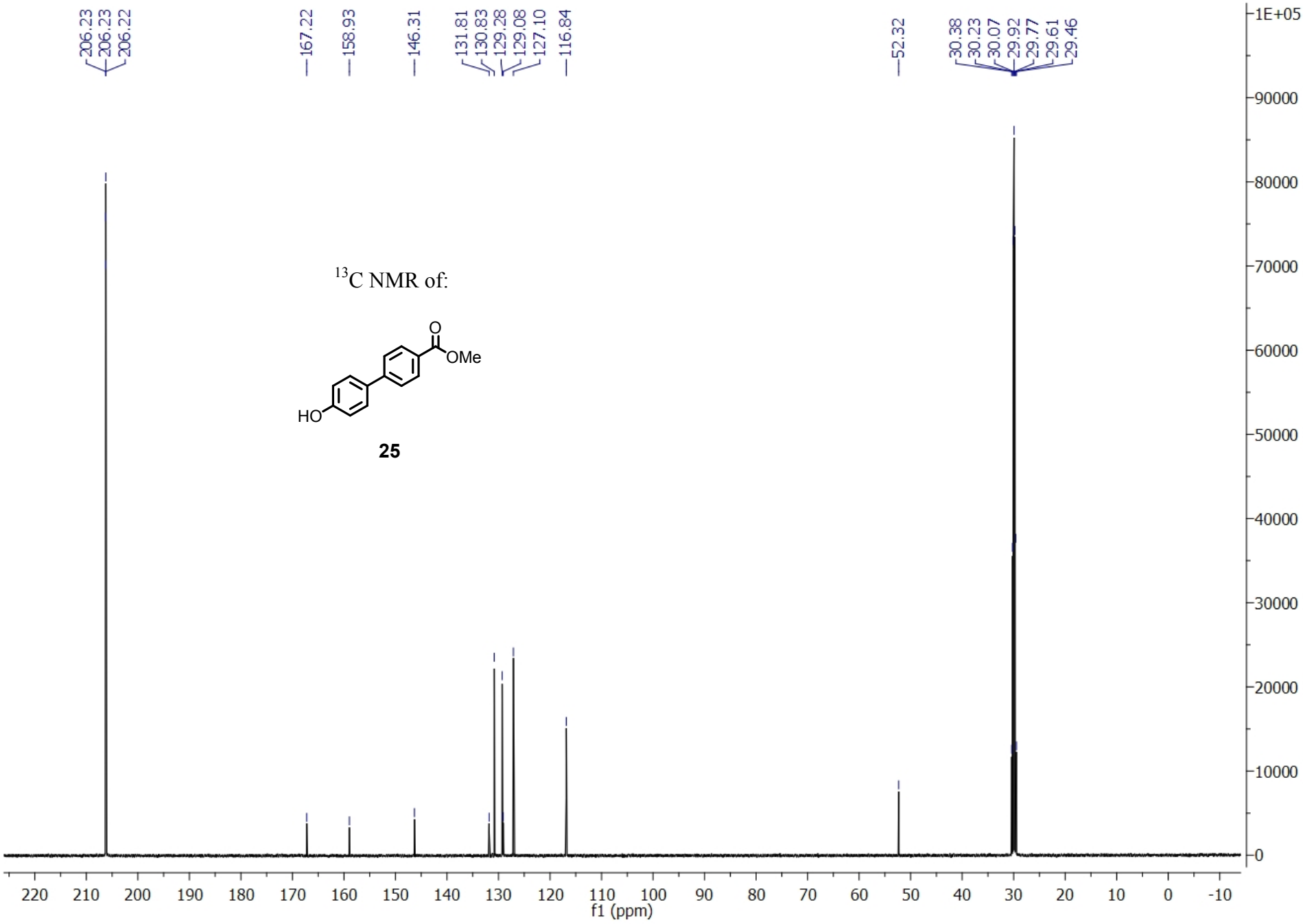
23

148.85
148.69
137.96
130.40
121.58
114.83
114.49
114.00
77.66
77.23
76.80
70.58
70.38
69.94
69.45
69.41
68.69
68.63
46.18
29.99
28.55
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

^{1}H NMR of:



25

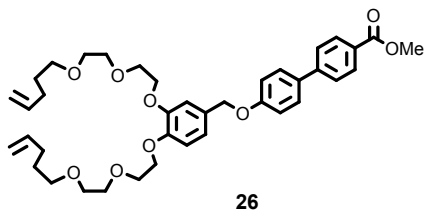

206.23
206.23
206.22
167.22
158.93
146.31
131.81
130.83
129.28
129.08
127.10
116.84
52.32
30.38
30.23
30.07
29.92
29.77
29.61
29.46
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{13}C NMR of:

O
OMe
HO

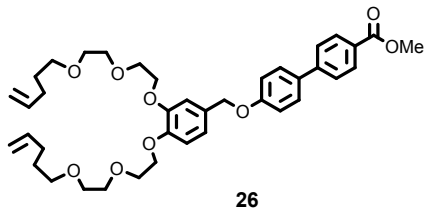
25

^{1}H NMR of:



26

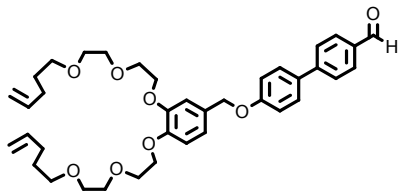
^{13}C NMR of:


O
OMe
O
O
O
O
O
O
O

26

167.22
159.16
149.24
149.00
145.32
138.43
132.73
130.26
128.52
128.38
126.63
121.09
115.46
114.89
114.77
114.42
77.65
77.23
76.81
71.04
70.93
70.36
70.17
69.90
69.11
69.07
52.26
30.41
28.94
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

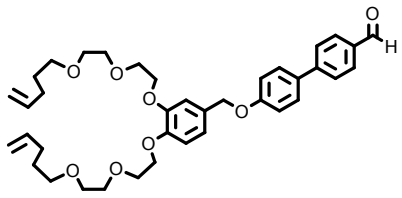
^{1}H NMR of:



27

21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
1.00
2.13
2.11
2.19
5.35
1.79
5.88
4.34
4.29
4.28
4.32
4.26
4.06
4.15
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

^{13}C NMR of:



27

192.04
159.42
149.27
149.05
146.87
138.41
130.46
130.01
128.64
127.20
121.09
115.55
114.88
114.81
114.47
77.65
77.23
76.81
71.03
70.91
70.35
70.17
69.89
69.13
69.10
30.39
28.93
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

CALIFORNIA INSTITUTE OF TECHNOLOGY

BECKMAN INSTITUTE

X-RAY CRYSTALLOGRAPHY LABORATORY

Date 2 June 2009

Crystal Structure Analysis of:

PGC05

(shown below)

For Investigator: Paul Clark ext. 6019

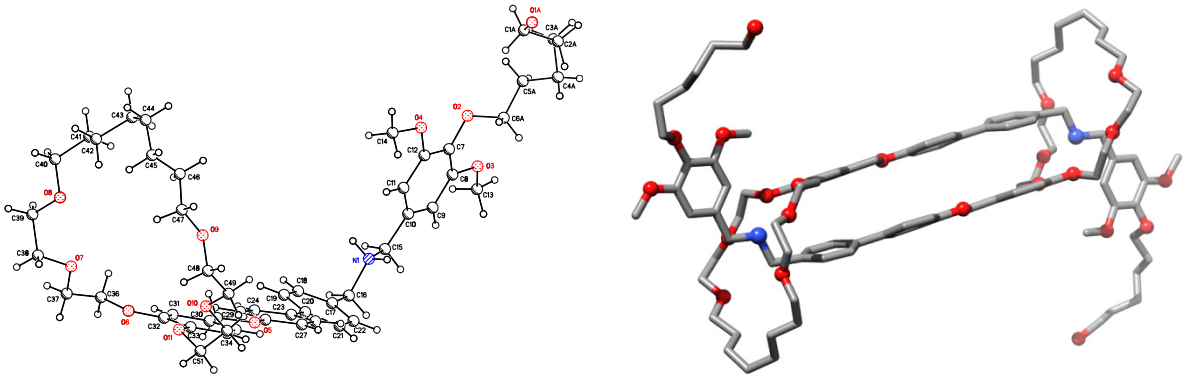
Advisor: R. H. Grubbs ext. 6003

Account Number: RHG.MTMCH3-1-NSF.MTMCH3

By Michael W. Day 116 Beckman ext. 2734

e-mail: mikeday@caltech.edu

Contents



PGC05

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC) and has been placed on hold pending further instructions from me. The deposition number is 734570. Ideally the CCDC would like the publication to contain a footnote of the type: "Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 734570."

Table 1. Crystal data and structure refinement for PGC05 (CCDC 734570).

Empirical formula	$[C_{51}H_{71}NO_{11}]^+$ (Hexafluorophosphate omitted)
Formula weight	874.09 (Hexafluorophosphate omitted)
Crystallization Solvent	Methanol/pentane
Crystal Habit	Plate
Crystal size	0.33 x 0.27 x 0.09 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	1.54178 Å CuKα
Data Collection Temperature	325(2) K
θ range for 5815 reflections used in lattice determination	3.30 to 60.52°
Unit cell dimensions	a = 32.5892(12) Å b = 15.3988(6) Å β= 124.734(3)° c = 28.4571(10) Å
Volume	11736.0(8) $Å^3$
Z	8
Crystal system	Monoclinic
Space group	C2/c
Density (calculated)	0.989 Mg/m^3 (Hexafluorophosphate omitted)
F(000)	3776 (1233 electrons recovered with SQUEEZE)
θ range for data collection	3.31 to 68.64°
Completeness to θ = 68.64°	87.2 %
Index ranges	$-37 \le h \le 36$, $-17 \le k \le 17$, $-32 \le l \le 32$
Data collection scan type	ω scans at 17 settings
Reflections collected	81248
Independent reflections	9453 [R_{int}= 0.1374]
Absorption coefficient	0.555 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9517 and 0.8379

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	9453 / 50 / 563
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.758
Final R indices [$I>2\sigma(I)$, 5289 reflections]	R1 = 0.1087, *w*R2 = 0.1987
R indices (all data)	R1 = 0.1521, *w*R2 = 0.2031
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.531 and -0.448 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

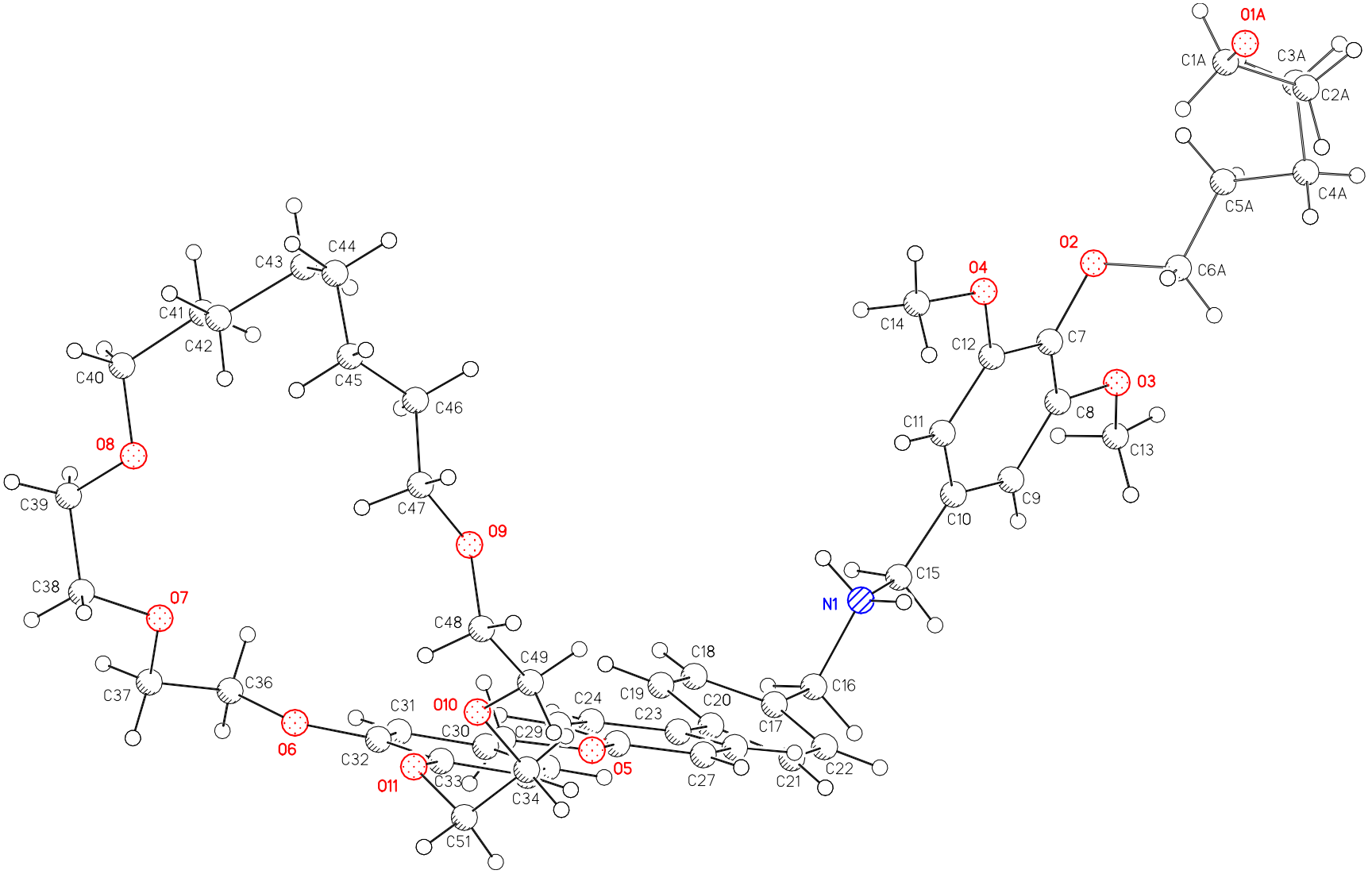
The hydroxy tail (O1-C6) is disordered and was modeled isotropically with geometry restraints.

All anions and possible solvent molecules were removed from the coordinates and the program SQUEEZE[1] was used to adjust intensities so as to account for electrons in the solvent region without including them explicitly as discrete atoms. Approximately 1152 electrons (eight hexafluorophosphates) were excluded in this way and 1233 were recovered by the program. These were NOT included in the molecular weight, calculated density or F(000).

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

[1] SQUEEZE - Sluis, P. v.d.; Spek, A. L. Acta Crystallogr., Sect A 1990, 46, 194-201.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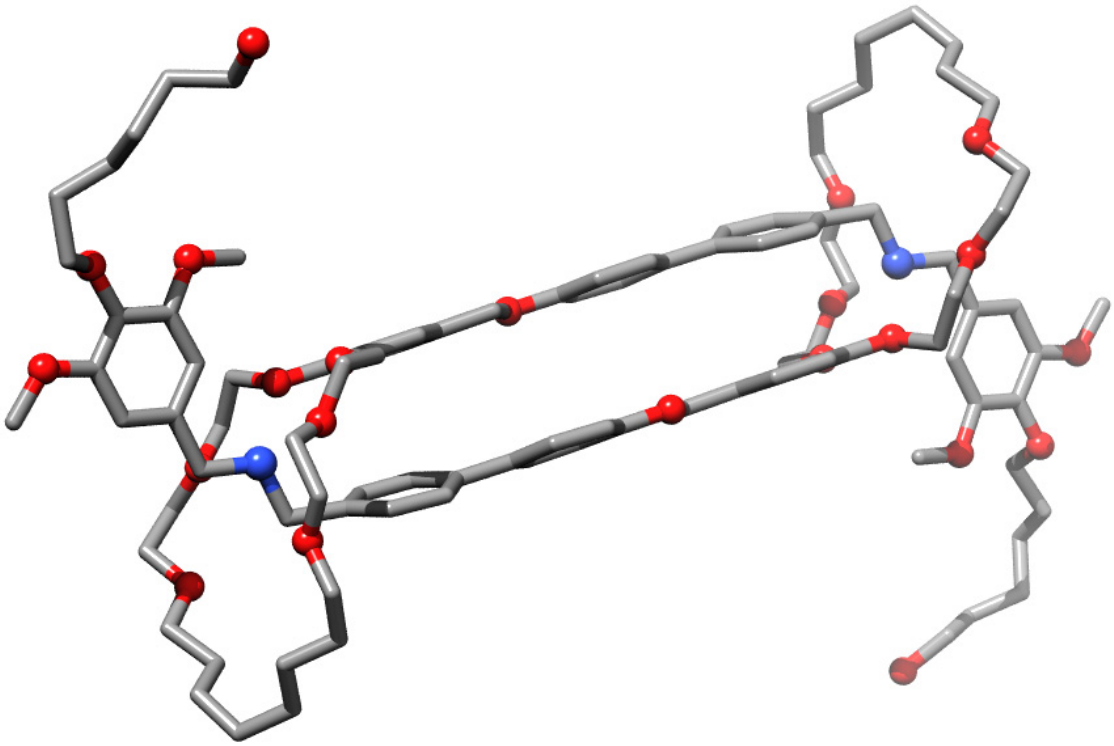

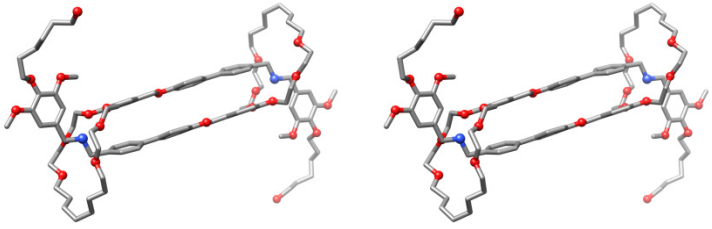

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for PGC05 (CCDC 734570) (CCDC 734570). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
O(2)	12490(1)	6303(2)	13885(1)	63(1)	1
O(3)	13286(2)	5579(2)	14833(2)	71(1)	1
O(4)	11907(1)	5388(2)	12930(1)	58(1)	1
O(5)	9658(1)	-1359(2)	10049(1)	60(1)	1
O(6)	8504(1)	-2676(2)	7600(1)	46(1)	1
O(7)	8217(1)	-2302(2)	6500(1)	59(1)	1
O(8)	7573(2)	-1117(3)	5575(2)	88(1)	1
O(9)	6075(2)	-1331(4)	6301(2)	99(2)	1
O(10)	6741(1)	-2620(3)	7159(2)	78(1)	1
O(11)	7806(1)	-2940(2)	7751(1)	51(1)	1
N(1)	12578(1)	2266(2)	13385(2)	43(1)	1
O(1A)	10079(11)	7968(19)	12404(15)	460(20)	0.50
C(1A)	10639(11)	7950(50)	12769(14)	650(30)	0.50
C(2A)	10852(7)	8090(30)	13389(12)	470(20)	0.50
C(3A)	11396(8)	8322(13)	13744(10)	299(15)	0.50
C(4A)	11688(6)	7628(12)	14185(8)	186(8)	0.50
C(5A)	12073(6)	7388(7)	14076(8)	115(6)	0.50
C(6A)	12133(4)	6426(7)	14051(6)	76(4)	0.50
O(1B)	10001(9)	7438(19)	13120(13)	387(14)	0.50
C(1B)	10388(10)	7180(40)	13020(20)	690(40)	0.50
C(2B)	10822(9)	7790(30)	13280(20)	570(20)	0.50
C(3B)	11308(8)	7480(30)	13795(13)	439(18)	0.50
C(4B)	11697(8)	7315(18)	13679(9)	286(13)	0.50
C(5B)	12213(8)	7466(12)	14205(12)	309(15)	0.50
C(6B)	12498(8)	6626(14)	14388(5)	213(10)	0.50
C(7)	12600(2)	5436(3)	13890(2)	47(1)	1
C(8)	13008(2)	5063(3)	14354(2)	47(1)	1
C(9)	13128(2)	4196(3)	14350(2)	44(1)	1
C(10)	12826(2)	3719(3)	13853(2)	41(1)	1
C(11)	12422(2)	4094(3)	13374(2)	45(1)	1
C(12)	12306(2)	4960(3)	13395(2)	47(1)	1
C(13)	13751(2)	5255(4)	15282(2)	85(2)	1
C(14)	11633(2)	4911(3)	12399(2)	70(2)	1
C(15)	12978(2)	2788(3)	13842(2)	47(1)	1
C(16)	12718(2)	1324(3)	13411(2)	45(1)	1
C(17)	12288(2)	832(3)	12913(2)	39(1)	1
C(18)	12229(2)	777(3)	12406(2)	41(1)	1
C(19)	11810(2)	398(3)	11932(2)	41(1)	1
C(20)	11436(2)	44(3)	11974(2)	36(1)	1
C(21)	11508(2)	68(3)	12502(2)	43(1)	1
C(22)	11930(2)	470(3)	12972(2)	45(1)	1
C(23)	10978(2)	-323(3)	11467(2)	35(1)	1
C(24)	10952(2)	-559(3)	10986(2)	45(1)	1
C(25)	10520(2)	-892(3)	10492(2)	49(1)	1
C(26)	10106(2)	-1021(3)	10508(2)	44(1)	1
C(27)	10111(2)	-804(4)	10973(2)	57(2)	1
C(28)	10537(2)	-441(4)	11447(2)	56(2)	1

C(29)	9641(2)	-1595(3)	9563(2)	51(1)	1
C(30)	9141(2)	-1933(3)	9104(2)	39(1)	1
C(31)	9080(2)	-2141(3)	8587(2)	47(1)	1
C(32)	8610(2)	-2481(3)	8137(2)	41(1)	1
C(33)	8238(2)	-2607(3)	8210(2)	47(1)	1
C(34)	8305(2)	-2395(3)	8730(2)	56(2)	1
C(35)	8767(2)	-2059(3)	9170(2)	56(2)	1
C(36)	8859(2)	-2467(3)	7483(2)	55(1)	1
C(37)	8676(2)	-2761(4)	6915(2)	61(2)	1
C(38)	8031(2)	-2422(4)	5911(2)	76(2)	1
C(39)	7951(2)	-1586(4)	5606(2)	78(2)	1
C(40)	7506(4)	-330(7)	5298(4)	148(4)	1
C(41)	7226(5)	358(7)	5396(4)	157(4)	1
C(42)	6704(4)	153(7)	5088(4)	149(4)	1
C(43)	6435(5)	847(8)	5221(5)	196(5)	1
C(44)	5887(5)	677(9)	4973(5)	218(7)	1
C(45)	5753(5)	-111(10)	5099(7)	253(8)	1
C(46)	5961(5)	-202(9)	5673(4)	181(6)	1
C(47)	5787(4)	-1062(9)	5720(4)	174(5)	1
C(48)	5928(2)	-2145(6)	6403(4)	117(3)	1
C(49)	6261(2)	-2338(4)	7006(4)	107(3)	1
C(50)	7053(2)	-2856(4)	7755(3)	77(2)	1
C(51)	7460(2)	-3376(4)	7836(2)	61(2)	1

Table 3. Bond lengths [Å] and angles [°] for PGC05 (CCDC 734570) (CCDC 734570).

O(2)-C(7)	1.380(5)	C(23)-C(24)	1.372(6)
O(2)-C(6A)	1.498(2)	C(23)-C(28)	1.417(6)
O(2)-C(6B)	1.501(2)	C(24)-C(25)	1.402(6)
O(3)-C(8)	1.378(5)	C(25)-C(26)	1.389(6)
O(3)-C(13)	1.404(6)	C(26)-C(27)	1.354(6)
O(4)-C(12)	1.384(5)	C(27)-C(28)	1.387(6)
O(4)-C(14)	1.443(5)	C(29)-C(30)	1.484(6)
O(5)-C(26)	1.392(5)	C(30)-C(35)	1.348(6)
O(5)-C(29)	1.401(5)	C(30)-C(31)	1.404(6)
O(6)-C(32)	1.393(5)	C(31)-C(32)	1.424(6)
O(6)-C(36)	1.412(5)	C(32)-C(33)	1.356(6)
O(7)-C(38)	1.433(6)	C(33)-C(34)	1.403(6)
O(7)-C(37)	1.455(5)	C(34)-C(35)	1.399(7)
O(8)-C(39)	1.385(7)	C(36)-C(37)	1.440(6)
O(8)-C(40)	1.393(8)	C(38)-C(39)	1.490(7)
O(9)-C(47)	1.420(10)	C(40)-C(41)	1.524(11)
O(9)-C(48)	1.432(8)	C(41)-C(42)	1.436(11)
O(10)-C(49)	1.433(6)	C(42)-C(43)	1.559(12)
O(10)-C(50)	1.442(6)	C(43)-C(44)	1.523(13)
O(11)-C(33)	1.361(5)	C(44)-C(45)	1.404(14)
O(11)-C(51)	1.446(5)	C(45)-C(46)	1.372(16)
N(1)-C(15)	1.451(5)	C(46)-C(47)	1.475(14)
N(1)-C(16)	1.510(5)	C(48)-C(49)	1.445(10)
O(1A)-C(1A)	1.501(2)	C(50)-C(51)	1.450(7)
C(1A)-C(2A)	1.500(2)		
C(2A)-C(3A)	1.500(2)	C(7)-O(2)-C(6A)	111.2(5)
C(3A)-C(4A)	1.503(2)	C(7)-O(2)-C(6B)	116.6(9)
C(4A)-C(5A)	1.501(2)	C(6A)-O(2)-C(6B)	41.5(9)
C(5A)-C(6A)	1.501(2)	C(8)-O(3)-C(13)	117.1(4)
O(1B)-C(1B)	1.500(2)	C(12)-O(4)-C(14)	116.3(4)
C(1B)-C(2B)	1.500(2)	C(26)-O(5)-C(29)	117.0(4)
C(2B)-C(3B)	1.500(2)	C(32)-O(6)-C(36)	118.9(4)
C(3B)-C(4B)	1.500(2)	C(38)-O(7)-C(37)	116.3(4)
C(4B)-C(5B)	1.501(2)	C(39)-O(8)-C(40)	109.8(6)
C(5B)-C(6B)	1.502(2)	C(47)-O(9)-C(48)	114.6(8)
C(7)-C(8)	1.358(7)	C(49)-O(10)-C(50)	110.5(5)
C(7)-C(12)	1.378(6)	C(33)-O(11)-C(51)	119.5(4)
C(8)-C(9)	1.393(6)	C(15)-N(1)-C(16)	113.4(3)
C(9)-C(10)	1.387(6)	C(2A)-C(1A)-O(1A)	112.1(14)
C(10)-C(11)	1.371(6)	C(1A)-C(2A)-C(3A)	113.9(14)
C(10)-C(15)	1.521(6)	C(2A)-C(3A)-C(4A)	109.6(13)
C(11)-C(12)	1.397(6)	C(5A)-C(4A)-C(3A)	102.0(10)
C(16)-C(17)	1.512(6)	C(4A)-C(5A)-C(6A)	113.5(10)
C(17)-C(18)	1.344(6)	O(2)-C(6A)-C(5A)	106.5(7)
C(17)-C(22)	1.385(6)	C(2B)-C(1B)-O(1B)	113.6(13)
C(18)-C(19)	1.387(6)	C(3B)-C(2B)-C(1B)	116.9(15)
C(19)-C(20)	1.403(6)	C(2B)-C(3B)-C(4B)	112.9(13)
C(20)-C(21)	1.382(6)	C(3B)-C(4B)-C(5B)	111.2(12)
C(20)-C(23)	1.473(6)	C(4B)-C(5B)-C(6B)	109.4(11)
C(21)-C(22)	1.403(6)	O(2)-C(6B)-C(5B)	106.5(10)

C(8)-C(7)-C(12)	119.6(5)	C(42)-C(41)-C(40)	111.1(10)
C(8)-C(7)-O(2)	121.5(5)	C(41)-C(42)-C(43)	109.6(10)
C(12)-C(7)-O(2)	118.7(5)	C(44)-C(43)-C(42)	116.3(11)
C(7)-C(8)-O(3)	116.5(5)	C(45)-C(44)-C(43)	118.9(13)
C(7)-C(8)-C(9)	121.4(5)	C(46)-C(45)-C(44)	112.2(17)
O(3)-C(8)-C(9)	122.0(5)	C(45)-C(46)-C(47)	104.1(13)
C(10)-C(9)-C(8)	118.5(5)	O(9)-C(47)-C(46)	109.5(9)
C(11)-C(10)-C(9)	120.8(5)	O(9)-C(48)-C(49)	108.0(6)
C(11)-C(10)-C(15)	121.1(4)	O(10)-C(49)-C(48)	112.0(7)
C(9)-C(10)-C(15)	118.0(4)	O(10)-C(50)-C(51)	107.2(5)
C(10)-C(11)-C(12)	119.3(5)	C(50)-C(51)-O(11)	116.5(5)
C(7)-C(12)-O(4)	116.8(5)		
C(7)-C(12)-C(11)	120.3(5)		
O(4)-C(12)-C(11)	122.9(5)		
N(1)-C(15)-C(10)	113.8(4)		
C(17)-C(16)-N(1)	110.1(4)		
C(18)-C(17)-C(22)	119.2(4)		
C(18)-C(17)-C(16)	121.8(5)		
C(22)-C(17)-C(16)	118.9(4)		
C(17)-C(18)-C(19)	122.0(5)		
C(18)-C(19)-C(20)	120.2(4)		
C(21)-C(20)-C(19)	117.6(4)		
C(21)-C(20)-C(23)	121.7(4)		
C(19)-C(20)-C(23)	120.7(4)		
C(20)-C(21)-C(22)	121.0(5)		
C(17)-C(22)-C(21)	119.9(4)		
C(24)-C(23)-C(28)	116.1(4)		
C(24)-C(23)-C(20)	122.1(4)		
C(28)-C(23)-C(20)	121.7(4)		
C(23)-C(24)-C(25)	123.5(5)		
C(26)-C(25)-C(24)	117.3(4)		
C(27)-C(26)-C(25)	121.7(4)		
C(27)-C(26)-O(5)	115.5(4)		
C(25)-C(26)-O(5)	122.8(4)		
C(26)-C(27)-C(28)	119.8(5)		
C(27)-C(28)-C(23)	121.4(5)		
O(5)-C(29)-C(30)	111.5(4)		
C(35)-C(30)-C(31)	120.8(5)		
C(35)-C(30)-C(29)	123.7(4)		
C(31)-C(30)-C(29)	115.5(4)		
C(30)-C(31)-C(32)	117.7(5)		
C(33)-C(32)-O(6)	116.9(4)		
C(33)-C(32)-C(31)	120.8(4)		
O(6)-C(32)-C(31)	122.3(5)		
C(32)-C(33)-O(11)	115.6(4)		
C(32)-C(33)-C(34)	120.8(5)		
O(11)-C(33)-C(34)	123.6(5)		
C(35)-C(34)-C(33)	118.1(5)		
C(30)-C(35)-C(34)	121.8(5)		
O(6)-C(36)-C(37)	108.7(4)		
C(36)-C(37)-O(7)	109.7(4)		
O(7)-C(38)-C(39)	112.7(5)		
O(8)-C(39)-C(38)	110.0(5)		
O(8)-C(40)-C(41)	114.9(8)		

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for PGC05 (CCDC 734570) (CCDC 734570). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	990(30)	410(20)	560(20)	-129(18)	490(20)	-70(20)
O(3)	860(30)	600(30)	640(30)	-270(20)	420(20)	-170(20)
O(4)	690(30)	440(20)	540(20)	63(19)	310(20)	90(20)
O(5)	430(20)	940(30)	360(20)	-123(19)	175(17)	-130(20)
O(6)	399(19)	480(20)	440(20)	-64(16)	196(17)	-97(17)
O(7)	580(20)	740(30)	420(20)	-68(19)	274(19)	-30(20)
O(8)	730(30)	1290(40)	620(30)	210(30)	370(20)	100(30)
O(9)	630(30)	1200(40)	760(30)	-200(30)	180(30)	50(30)
O(10)	570(30)	750(30)	930(30)	-260(20)	380(20)	-180(20)
O(11)	440(20)	540(20)	420(20)	-71(17)	171(18)	-116(18)
N(1)	400(20)	370(20)	400(20)	-95(19)	160(20)	-50(20)
C(7)	680(40)	330(30)	460(30)	-70(30)	350(30)	-40(30)
C(8)	570(30)	470(30)	450(30)	-240(30)	340(30)	-250(30)
C(9)	360(30)	530(30)	440(30)	-80(30)	240(20)	-90(30)
C(10)	400(30)	420(30)	420(30)	-90(20)	240(30)	-80(30)
C(11)	440(30)	380(30)	380(30)	-110(20)	140(20)	-80(30)
C(12)	550(30)	420(30)	530(30)	0(30)	360(30)	-20(30)
C(13)	660(40)	1000(50)	630(40)	-430(40)	210(40)	-160(40)
C(14)	720(40)	570(40)	530(40)	80(30)	180(30)	10(30)
C(15)	320(30)	470(30)	430(30)	-140(20)	100(20)	-50(30)
C(16)	340(30)	350(30)	490(30)	-10(20)	130(20)	40(20)
C(17)	340(30)	320(30)	400(30)	-30(20)	150(20)	-10(20)
C(18)	350(30)	380(30)	430(30)	-30(20)	180(20)	-50(20)
C(19)	440(30)	370(30)	420(30)	10(20)	240(20)	60(30)
C(20)	430(30)	250(30)	350(30)	-50(20)	190(20)	10(20)
C(21)	460(30)	460(30)	410(30)	-20(20)	260(30)	-100(30)
C(22)	520(30)	370(30)	300(30)	-30(20)	150(20)	-50(30)
C(23)	300(30)	340(30)	400(30)	30(20)	190(20)	0(20)
C(24)	410(30)	540(30)	440(30)	-90(30)	270(30)	-120(30)
C(25)	440(30)	660(40)	330(30)	-100(30)	200(30)	-60(30)
C(26)	350(30)	540(30)	240(30)	-70(20)	50(20)	-70(30)
C(27)	300(30)	970(50)	370(30)	-40(30)	160(20)	-90(30)
C(28)	470(30)	850(40)	340(30)	-120(30)	210(30)	-60(30)
C(29)	490(30)	590(40)	400(30)	-80(30)	210(30)	-10(30)
C(30)	390(30)	400(30)	300(30)	-70(20)	150(20)	-100(20)
C(31)	400(30)	490(30)	400(30)	-20(20)	160(20)	40(30)
C(32)	430(30)	330(30)	340(30)	-60(20)	140(20)	-10(20)
C(33)	520(30)	420(30)	400(30)	-40(20)	230(30)	-90(30)
C(34)	680(40)	550(40)	500(30)	-50(30)	370(30)	-60(30)
C(35)	640(40)	540(40)	400(30)	-80(30)	230(30)	-20(30)
C(36)	520(30)	640(40)	450(30)	-30(30)	250(30)	40(30)
C(37)	530(30)	750(40)	610(40)	10(30)	370(30)	80(30)
C(38)	710(40)	990(50)	640(40)	-270(40)	420(40)	-290(40)
C(39)	720(40)	1010(60)	570(40)	10(40)	350(40)	-160(40)
C(40)	1880(100)	1380(90)	1260(80)	610(70)	940(80)	350(80)
C(41)	1890(120)	1330(90)	1070(80)	210(70)	590(80)	10(90)
C(42)	1300(90)	1490(100)	1110(80)	-330(70)	340(70)	-140(80)

C(43)	1470(110)	2110(140)	2020(120)	-670(110)	820(100)	-180(100)
C(44)	1800(140)	1690(130)	1790(120)	310(100)	270(100)	-50(120)
C(45)	2060(160)	2100(170)	2800(200)	720(170)	1030(160)	570(140)
C(46)	1510(100)	2360(150)	750(70)	660(90)	170(70)	390(100)
C(47)	1270(90)	2680(160)	770(70)	-360(90)	290(70)	590(100)
C(48)	470(40)	870(60)	1520(80)	-490(60)	190(50)	-100(40)
C(49)	650(50)	700(50)	1990(90)	-360(60)	840(60)	-150(40)
C(50)	680(40)	830(50)	730(40)	-230(40)	360(40)	-250(40)
C(51)	670(40)	630(40)	650(40)	10(30)	450(30)	-100(30)

Table 5. Hydrogen bonds for PGC05 (CCDC 734570) (CCDC 734570) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1AA)...O(11)#1	0.90	2.02	2.914(5)	172.2
N(1)-H(1AB)...O(7)#1	0.90	1.90	2.793(5)	174.8